

# Kumamoto Journal of Science

Series A (Mathematics, Physics and Chemistry)

---

Vol. 1, No. 4, March 1954

---

Published by the  
Faculty of Science, Kumamoto University  
Kumamoto, Japan

熊本大學理學部紀要 第一部 第一卷 第四號 昭和二十九年三月

熊 本 大 學 理 學 部

Kumamoto Journal of Science

Series A (Mathematics, Physics and Chemistry)

Digitized by the Internet Archive  
in 2025

# SOME STUDIES ON VOLCANO ASO AND KUJIU, (PART, 8.) A CONSIDERATION ON THE PROCESS OF EARTHQUAKE FREQUENCY FOLLOWED BY A VOLCANIC EXPLOSION.

Munetoshi NAMBA.

(Received on January 31, 1954.)

## Abstract.

The writer should like to discuss a trial about some co-relation between the underground volcanic explosion and the surface eruption in the case when volcanic explosion occurs. He fortunately could make some progress in his trial, and found that some preliminary tremors, main shock, and after shocks must generally follow to a volcanic earthquake caused by a volcanic intrusion.

## 1. Forewords.

The writer studied the process of volcanic explosion in the last paper [1], and in the present paper, according to the result of the study, should like to discuss a trial about the co-relation between the underground volcanic explosion and surface eruption by researching the case when volcanic explosion occurs, and about the connexion among preliminary tremor, main shock, and after shocks of a volcanic earthquake. Prior to the surface eruption, motive power of explosion causes severe or weak shocks of a volcanic earthquake.

The time lag emitting of smoke from the first shock of underground eruption (volcanic earthquake) varies in each several volcanoes. About this topic the late Prof. Omori said as follows [2].

(1). In the case when Bondaisan exploded in the 21st year of Meizi (1888), the time lag was only ten minutes or so.

(2). Time difference between the first shock of volcanic earthquake and emitting of smoke in Miyakejima (Kansei, syotoku, Hōreki, Tempo, and 1874), Usudake (1663, 1858, and 1910), and Sakurazima (1779, 1914), was several hours or days; and the volcano began to erupt after some times from the time when a Volcanic earthquake suddenly increased in number and reached to the maximum frequency.

(3). Time difference between the first shock of earthquake and emitting of smoke in Unzendake (1792), Kirishimayama (1903). and Asamayama (1913) was several months or a year.

In this case the volcanic earthquake, as the case may be, increase in frequency and is very severe for a while, but it is after several days from the time when it became still for once that the volcano begins to erupt.



(4). Except the above mentioned instances, there are great many other ones that a volcano is restored to its normal state without any explosion after a volcanic earthquake increased in frequency and was very severe. (The rumbling of Arima Hot Spring on July of 1899, the Kinpozan Earthquake on June of 1943, and etc.).

Upon this, the writer took up "Volcanic Activity under the surface of the earth" as a solution for these phenomena.

In such a case when volcanic activity takes place under the surface of the earth, in every activity in both the boring and magma stage the earthquakes occur instead of explosive sounds; and if the earthquake is very weak, microtremors only appear without saying.

For the present, we will regard this process as that after the resistance of a plug of a volcanic conduit tube is excluded by foreshock, magma is then pushed up by the after shock "for the sake of mathematical treatment".

## 2. An Earthquake in the Boring Stage (Foreshock in Short).

An explosive power in the boring stage affects as boring pressure. If  $p$  is the boring pressure,  $R$  is the resistance of a plug of a volcanic conduit tube,  $N$  is the number of foreshock, and  $t$  is the time, we shall profit by the result of the observation of the number of explosion as it is stands.

$$\left. \begin{aligned} N &= \frac{1}{cP_0 - b/R_0} \sqrt{\frac{1}{(cP_0 - b/R_0)^2} - \frac{2aP_0}{R_0(cP_0 - b/R_0)t}} \\ \frac{dN}{dt} &= \frac{aP_0}{R_0} \left\{ 1 - \frac{2aP_0}{R_0} (cP_0 - b/R_0)t \right\}^{-\frac{1}{2}} \end{aligned} \right\} \dots\dots\dots (1)$$

in which  $(cP_0 + b/R_0)$   $N$  is very small;  $cR_0 > b/R_0$ ;  $a$ ,  $b$ ,  $c$ , are some constants; and  $p_0$ ,  $R_0$  are values of  $P$ ,  $R$  at the time when  $t$  is zero. Therefore, at the time when

$$t = \frac{R_0}{2aP_0(cP_0 - b/R_0)} \equiv \tau \dots\dots\dots (2)$$

$dN/dt$  becomes at the maximum, and, at the same time, the boring stage comes to an end. And it follows as

$$\left. \begin{aligned} -\frac{dP}{dN} &= \frac{bP_0}{R_0} \left\{ 1 - \frac{2aP_0}{R_0} \left( cP_0 - \frac{b}{R_0} \right) t \right\}^{-\frac{1}{2}} \\ -\frac{dP}{dt} &= \frac{abP_0^2}{R_0^2} \left\{ 1 - \frac{2aP_0}{R_0} \left( cP_0 - \frac{b}{R_0} \right) t \right\}^{-1} \end{aligned} \right\} \dots\dots\dots (3)$$

The characters of  $N$ ,  $dN/dt$  is all the same as that of the numbers of surface explosion, and the value of  $R$ ,  $P$  at the time when  $t = \tau$ , is  $R_\tau$ ,  $P_\tau$  respectively, and the pressure in the boring stage is scarcely consumed.

Intensity of the foreshock is represented by equation (3).

### 3. An Earthquake in the Magma Stage (after shock in short).

If  $n$  is the number of earthquake in the magma stage we can make use of the result in the case of the surface explosion as it is stands.

$$\left. \begin{aligned} n &= \frac{-1}{\frac{\beta}{R_\tau} - \gamma P_\tau} + \sqrt{\frac{1}{\left(\frac{\beta}{R_\tau} - \gamma P_\tau\right)^2} + \frac{2 \cdot \alpha \cdot P_\tau \cdot t}{R_\tau \left(\frac{\beta}{R_\tau} - \gamma P_\tau\right)}} \\ \frac{dn}{dt} &= \frac{\alpha \cdot P_\tau}{R_\tau} \left\{ 1 + \frac{2 \cdot \alpha \cdot P_\tau}{R_\tau} \left( \frac{\beta}{R_\tau} - \gamma P_\tau \right) t \right\}^{-\frac{1}{2}} \end{aligned} \right\} \dots\dots\dots (4)$$

in which  $(\beta/R_\tau + \gamma P_\tau) n$  is very small and  $\beta/R_\tau > \gamma P_\tau$ ;  $\alpha, \beta, \gamma$  are some constants; and  $P_\tau$  and  $R_\tau$  are the values of  $P$  and  $R$  respectively at the time when boring stage terminated.

Therefore,

$$\left. \begin{aligned} P_{t \rightarrow \infty} &= 0, \quad R_{t \rightarrow \infty} = \frac{\beta}{\beta/R_\tau - \gamma P_\tau}; \\ -\frac{dP}{dn} &= \beta \frac{P_\tau}{R_\tau} \left\{ 1 + \frac{2\alpha P_\tau}{R_\tau} \left( \frac{\beta}{R_\tau} - \gamma P_\tau \right) t \right\}^{-\frac{1}{2}} \\ -\frac{dP}{dt} &= \alpha \cdot \beta \frac{P_\tau^2}{R_\tau^2} \left\{ 1 + \frac{2\alpha P_\tau}{R_\tau} \left( \frac{\beta}{R_\tau} - \gamma P_\tau \right) t \right\}^{-1} \end{aligned} \right\} \dots\dots\dots (5)$$

The characters of  $n$ ,  $dn/dt$  are all the same as that in the case of surface explosions.

Intensity of the magma stage earthquake is represented by (5).

### 4. Result of Study (1).

(Relation between a surface eruption and a volcanic earthquake).

(A).  $N$ ,  $dN/dt$  in the equation (1) for the foreshock coincides with the result of observation for the most part.

Figure 1 illustrates the volcanic earthquake at the time when Usudake exploded in the year of 1910 [3].

(B). Each strength of volcanic earthquakes are expected to be direct proportion to  $-dP/dN$ ,  $-dP/dn$ .

In view of this fact, foreshock gradually increases in strength with the lapse of time, and become maximum at  $t$  is  $\tau$ .

Number and frequency of foreshock are convex to  $t$ -axis.

The aftershock, on the contrary, is the severest in the beginning and decreases in turn with the lapse of time; frequency of aftershock are convex to  $t$ -axis.

It is clear that they are the severest in the strength and the maximum in its frequency.

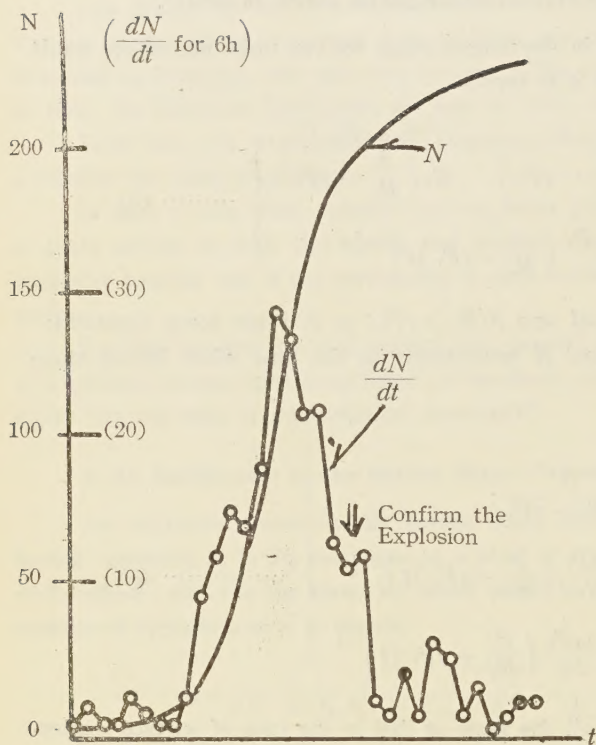


Fig. 1 Volcanic Earthquake in USU-dake (1910) and its frequency per 6 hours.

The mean amplitude per unit time, as is clear from the equation (3) and (5), is convex to  $t$ -axis and reaches to the greatest value at the time when  $t$  is  $\tau$  in both the boring and magma stages.

It is matter of course that the curve is more steep before and after  $t$  is  $\tau$  rather than  $dN/dt$ ,  $dn/dt$ .

Figure 2 is the curve of mean amplitude per hour.

This curve shows the activity of the origin from which the one-second period vibration emits at the time when the fourth crater of Aso Volcano exploded on September of 1930 [4].

The curves are more distinct than the frequency of the number of a microtremor of the volcanic earthquake.

(E). When volcanic activity enters into the magma stage in an interusion, a large quantity of volcanic gas is congested directly below the bottom of a crater, and a smoke begins to gush out from the upper part of a volcanic conduit tube; this is so-called boring stage in surface eruption.

ney before and after  $\tau$ .

(C). Since they increase in frequency and strength in proportion to approach  $t$  to  $\tau$ , it is just and reasonable that we feel as if  $dN/dt$  in foreshock increases very quickly before and after  $t$  is  $\tau$ ; and, in aftershock, on the contrary, decreases quickly after  $t$  is  $\tau$  on a settled seismometer.

(D). In an activity of Vesuvian type of which underground volcanic activity is comparatively calm, there must be cases when it is difficult to calculate the numbers of the volcanic earthquakes.

In such a case, it must be more easy to measure the mean amplitude per unit time ( $-\frac{dp}{dt}$ ) than count up the number (such as  $-dN/dt$  and  $-dn/dt$ ) or measure the average of each amplitude (as  $-dP/dN$  and  $-dp/dn$ ).



With the lapse of time it progresses in the magma stage in the surface eruption and sends out black clouds furiously until it arrives at the most vigorous active stage.

Therefore even an observer at a great distance can confirm volcanic explosion.

Thinking these series of phenomenon, we can measure volcanic explosion as it exploded after several hours of the maximum frequency or the maximum amplitude of a microtremor of the volcanic earthquake.

Depending upon the writer's experience that he did at the first crater of Aso Volcano, the initiatory period of the boring stage in a surface eruption is unable to confirm by an observer at a long distance, but one at the actual crater can clearly confirm it.

In a great many records about eruption, and, especially, even in the record about the Volcanic Activity of Volcano Type as Bandainsan, there is description that the white smoke rising into the atmosphere is seen before the time when the volcano is recorded as its explosion.

At the time when the second crater of Aso Volcano exploded on February 24th of the year 1933, it has already been active in the evening of 23rd actually; this is why the dwellers near the crater went down the volcano to take refuge in the middle of the night.

On the contrary at San-jiyo-Hondo (about 800 meters west from the crater) the explosion could be confirmed for the first time about half past two o'clock of February 24th.

Such being the fact, one has no objection to judge that the surface eruption already began when, at least,  $t$  is  $\tau$ .

For this reason we have no objection to say that time difference between the beginning of a volcanic earthquake (equation 1,2) and spouting of smoke, corresponds to the time lapse of the boring stage in a surface eruption.

(F). When an intrusion is acted in a considerably deep place under the bottom of a crater, as the case may be, volcanic gas pressure can not exclude the plug of a volcanic conduit tube,  $dN/dt$  or mean amplitude of microtremors become greater and greater, and

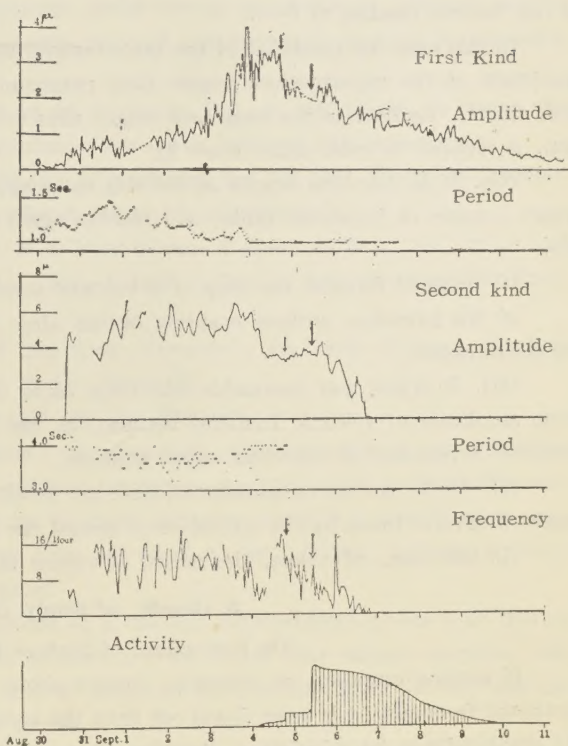


Fig. 2. Mean amplitude of microtremor (First kind) in Aso Explosion (1931) observed by Dr. K. Sassa.

at last the time reaches to  $t=\tau$ .

In this case the condition of the crater is still unchanged, but the frequency or mean amplitude of the microtremors passes their maximum, develops into the magma stage, and, finally, declines in the consumed stage; thus volcanic activity, without surface eruption, is reduced in order again (case 4).

(G). If an intrusion begins at the still more upper part, the quiet volcano for once causes a series of foreshock again, and reaches again to the time of the maximum frequency.

If, by good fortune, the plug of a volcanic conduit tube can be excluded as a result of this intrusion, surface eruption occurs after time of the maximum frequency of the microtremor.

(H). It is just and reasonable that there come out other maximum in frequency or mean amplitude of volcanic tremors, because, as has been previously mentioned, another intrusion is repeated at the other upper stratum.

(I). Under certain circumstances, there are possibilities that the surface eruptions were repeated several times by the intrusions at almost the same stratum.

(In this case, of course, the period of tremor may differ in the case of (H)).

## 5. Result of Study (2).

(On Foretelling of Surface Eruption).

If surface eruption, in principle, begins about time when the foreshock is at the maximum frequency,  $t$  is to be found out from the curve of  $dN/dt$ ,  $t$ , or from the equation (1) graphically or by calculating; therefore it must be expected to foresee the expectant hour in general.

An example is depicted in Figure 3.

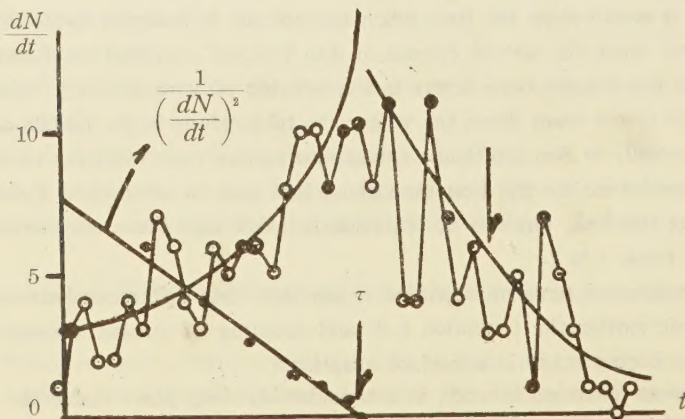


Fig. 3. Frequency and  $1/\left(\frac{dN}{dt}\right)^2$  per 2 hours in the case of Volcano Sakura-Shima (1914).



But, as has been previously mentioned, under certain circumstances, volcanic activity can not cause a surface eruption because the place of a subterranean eruption is comparatively deep.

Then we must know the depth of an intrusion, but, to our regret, to sound the depth of the place of a subterranean explosion has never been put into operation.

For this attempt the writer should like to remember the fact that "Period of a tremor wave, observed by distance from the seismic center, is at variance".

At Volcano Asama microtremor of 5.7sec, 2.1sec, 0.82sec, 0.39sec, are found and at Volcano Usu-dake and Miharayama 0.52sec, 1.1sec, 1.6sec, 2.1sec are found by Prof. Ōmori.

At Volcano Aso microtremor of 2nd Kind (4-6sec.), 4th kind (0.2sec.), 1st kind (1sec.), 3rd kind (0.5sec.) are founded by Dr. Sassa [7].

At Miharayama 1.1sec predominated (by Dr. Nagata).

These facts show that, as is common to nation-wide, a fitting place to cause an intrusion (from which 1.5 second period volcanic microtremor emits) exists in the earthcrust.

Besides, we know that some of the volcanic intrusions occur in a considerably deep place inferring from the fact that there were period of 26.4sec, 6.0sec, 0.95sec, 0.38sec, and etc. among the volcanic microtremors.

The time of the maximum amplitude of a volcanic microtremors moves from that of long period to short one by degree till volcanic activity enters into surface eruption; and that the period of tremor in volcanic activity is almost fixed kinds shows the fact that the depth of an intrusion source is almost settled.

But an intrusion source of one second period tremor or so, which is regarded as a very conspicuous source of a volcanic intrusion in our country, as we often experience, not always causes surface eruption; in Volcano Aso, for instance, there are many examples that an intrusion source of one second period or so did not cause a surface eruption even when the first grade of a microtremor of a volcanic earthquake began to fall, in its amplitude, that is, even after the first grade of a microtremor passed  $\tau$ . [8]

This fact tells us that a final intrusion source for a surface eruption is still more upper part than an intrusion source for one second period or so.

An intrusion source for the third grade of a microtremor is likely to wear an aspect of certainty in Aso.

This gives an account of this condition [9].

The writer declares without hesitation that, in any case, when a volcanic intrusion takes place in an intrusion source for more shorter period than one second, the volcano always go into surface eruption.

The depth of an volcanic intrusion source, measured on the year of 1933 at Volcano Aso is said about 1000 meters in depth under the bottom of the first crater.

The minute observation of the depth of an volcanic intrusion source is the future problem.

### 6. On Preliminary Tremor.

There are preliminary tremor, main shock, and after shocks in seismic phenomenon, but the co-relation among them is not yet clear except the following five facts [10].

(1). A severe earthquake without preliminary tremor is always accompanied by the after shocks.

(2). A severe earthquake without preliminary tremor is always attended with after shocks, too.

(3). An earthquake follows the rumbling of the ground is comparatively severe earthquake, and, as the case may be, it is accompanied or is not accompanied by after shocks.

(4). There are earthquakes that have only main shock, and, as the case may be, is accompanied or is not accompanied by after shocks.

(5). There are volcanic earthquakes that come to an end with the rumbling of the ground or phenomenon of frequent occurrence of a slight shock.

By Prof. Ōmori and Matsuyama's observations, preliminary tremor, at the beginning, is considerably severe, and secondary a slight shock of volcanic earthquake occurs frequently till it enters into main shock, but there is no final material to explain the co-relation between preliminary tremor and main shock.

The writer should like to recall the process of volcanic earthquakes caused by volcanic intrusion, which he mentioned in the present paper, and should make this a solution to solve the question.

This idea is to regard a boring-stage-shock as preliminary tremor, the severest shock before and after  $\tau$  as the main shock, and the magma-stage-shock as a phenomenon of after shock.

Then, for the first time, we can understand the above mentioned all items for the depth of a volcanic intrusion and magnitudes of each constants in the original equation; it is without saying that a seismic phenomenon is due to various causes, but, to say the least of it, the all items of a volcanic earthquake caused by intrusion are perfectly cleared.

The data of preliminary tremor is not enough and we must expect the quantitative study in future, but on after shocks, there are Ōmori, Kusakabe, and Matsuyama's results of study.

By Prof. Ōmori's study, it is said that his experimental formula perfectly coincides with an observed data; that is, if  $y$  is Number of after shock in a certain time, after a main earthquake, Nōbi-earthquake, for instance, is shown by the equation,  $y = K/(x+h)$  and for the Nōbi-earthquake that occurred on October 29th of the year of 1891,  $K=440.7$   $h=2.314$ .

Kumamoto-earthquake that occurred on July 28th of 1889 more perfectly coincides with the equation,  $y = \frac{k}{\alpha + \beta t + \gamma t^2}$ .

About the former equation there are Enya's theoretical solution and Prof. Matsuyama's one [11]. [12]

About the latter there is Enya's one, but he used another idea, because the solutions

were irrational in conclusion. [13]

Now, expanding the equation of a magma stage (4) and taking the term till  $t^2$  according to the present writer's ideal, it coincides to the equation by Nobi-earthquake; if he puts up in the original formula.

$$\left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right)^n \gg \log \frac{\gamma P_{\tau} R_{\tau}}{\beta}, \text{ then } e^{\left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right)^n \div 1 + \frac{\alpha \left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right)^3}{\gamma^3 P_{\tau} R_{\tau}}} t$$

therefor,

$$\frac{dn}{dt} = \frac{1}{t + \frac{\gamma^3 P_{\tau} R_{\tau}}{\alpha \left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right)^3}} \left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right) \dots \dots \dots (8)$$

$$\text{Therefore we have } K = \frac{1}{\gamma P_{\tau} + \frac{\beta}{R_{\tau}}} \text{ and } h = \frac{\gamma^3 P_{\tau} R_{\tau}}{\alpha \left(\gamma P_{\tau} + \frac{\beta}{R_{\tau}}\right)^3}$$

for Ōmori's constants.

This result just coincides with Ōmori's experimental formula and Matsuyama's theoretical one.

The above Kumamoto-earthquake which occurred in Volcano Kimpōsan region is a volcanic earthquake that occurred at the source of a volcanic activity of Volcano Kimpōsan. This corresponds with the case of a volcanic intrusion that the writer is turning over in his mind.

Result of the actual observation is  $\int_0^{t-1} \frac{dn}{dt} dt$ , which, does not particularly differ from  $\frac{dn}{dt}$  as is admitted by Prof. Matsuyama and Enya's ideas. [14]

It seems to the writer that a volcanic earthquake caused by volcanic intrusion, in generally, always passes from preliminary tremor to main shock at the time when  $t$  is  $\tau$ , and, finally, is attended with after shocks.

Especially in the case of the comparatively shallow intrusion of a Vesuvian Type, the rumbling of the ground and microtremors of whose period is very short, frequently occur, but they often come to an end without developing into a severe earthquake.

They say that a green pheasant and a catfish forebode an earthquake, and the records that a microtremor often gets particular people to feel a flash of light are left.

A hunter and a fisher have turned their attention, in particular, to the fact that a green pheasant and a catfish are more sensitive to a slight vibration of the ground than to a sound-waves; to take into consideration the case, that an earthquake caused by a



volcanic intrusion is resonant with a green pheasant and a catfish even at the time when the preliminary tremor is too weak to have the human body feel a shock, it is not impeded to think that a slight shock of an earthquake make a man with an acute sensitivity like as a possessor of a special retina feel a flash of light even in dark night.

But on preliminary tremor the writer is obliged to relate beyond this in future for insufficiency of the data,

### 7. Conclusion.

The writer has treated the relation between surface explosion and a microtremor of a volcanic earthquake; mean amplitude of microtremor, the frequency of a slight shock by the subterranean volcanic activity or volcanic intrusion are treated.

The possibility of forecasting of surface explosion is remembered seismological point of view by using an apparatus that is resonant with a vibration of whose period is more shorter than one second.

The writer found the facts that preliminary tremor, main shock and after shocks must generally follow to a volcanic earthquake caused by a volcanic intrusion.

### Litteratures.

- [1]. Namba: --some studies on Volcano Aso and Kujiu (part 6).  
A consideration on the process of Sounds by a volcanic explosion; read on Japan Physical Society, 1943;  
This Journal. Aug. 1953.
- [2]. F. Ōmori: -- generation of Earthquake by a volcanic explosion: --  
Bulletin of the Imperial Earthquake Inves. commtee, vol.87. p.54.
- [3]. F. Ōmori: -- ditto to [2].
- [4]. K. Sassa: -- Memoir of Kyoto Imp. Univ. Series A, vol. 18 (1935), p.255.  
Chikiu-butsuri vol.3 No.3 (1939), p.15. vol.19. (1936), p.11.
- [5]. M. Namba: --co-relation between a volcanic explosion of Aso and gradient of vertical Earth-current; Memoir of Kyoto Imp. Univ. Series A; vol.23 (1941), p.171.  
Chikiu-butsuri, vol.3, No.4 (1935), p.301. etc.
- [6]. F. Ōmori: --Volcanic Calender of Japan; vol.11, p.44.
- [7]. K. Sassa: -- on the property of a volcanic microtremor and explosive shock; Chikiu-butsuri, vol.3. No.2. (1939), p.142.
- [8]. An example; K. Sassa: --ditto [4].  
On foretelling of the explosion of Volcano Aso;  
Volcano: vol. 3, No.2. (1937), p. 125, (Bulletin of volcanological Society of Japan).
- [9]. Ditto. [4].
- [10]. F. Ōmori: --Reports on after-shock, Bulletin of Imp. Earthquake comm.; vol.2, No.30.  
K. Matsuyama: --Recent Seismology (1925).  
A. Imamura: --On Seismology (1924).  
K. Wadachi: -- Earthquake (Sinsai part 1), (1935).
- [11]. O. Enya: -- On the aftor-shock; Bulletin of Imp. earthquake comm.; vol.35, p.35.
- [12]. Ditto.
- [13]. Ditto [11].
- [14]. Ditto [both].

# ON THE SENSITIVITY OF WHEATSTONE BRIDGE

Ryuzo ADACHI

The article discusses the sensitivity of wheatstone bridge, and under certain conditions, finds the arm resistances which give the highest sensitivity, and some special cases are mentioned.

## 1. Introduction

Suppose a wheatstone bridge as shown in Fig. 1., and let  $i_g$  be the current which passes the galvanometer. The sensitivity  $S_r$  of the bridge referred to  $r$  may be defined as

$$S_r = \lim_{\partial r \rightarrow 0} \left| \frac{\partial i_g}{\partial r} \right| = \left| r \frac{\partial i_g}{\partial r} \right|.$$

Similarly  $S_x$ ,  $S_y$ ,  $S_z$  are defined.

If the bridge is balanced, we can introduce following relations

$$xy = zr \dots \dots \dots (1)$$

$$i_1 = \frac{x E}{x(y+r) + \rho(x+r)}, \quad i_2 = \frac{r E}{x(y+r) + \rho(x+r)} \dots \dots \dots (2)$$

$$S_x = S_y = S_z = S_r = \frac{r E}{J} = S \dots \dots \dots (3)$$

where

$$J = \left( x + r + g + \frac{g}{y} r \right) \left( y + r + \rho + \frac{\rho}{x} r \right) \dots \dots \dots (4).$$

In the following section, let  $r$  be a given resistance which is measured and  $x$ ,  $y$  be some resistances which are determined suitably so as to obtain high precision. When  $r$ ,  $E$  are given, it is obvious that  $S$  is largest when  $J$  is least.

## 2. Highest Sensitivity when $\rho=0$

If  $\rho=0$ , we have

$$i_1 = \frac{E}{y+r}, \quad i_2 = \frac{r E}{x(y+r)} \dots \dots \dots (2)$$

$$J = (y+r) \left( x + r + g + \frac{g}{y} r \right) \dots \dots \dots (4)'$$

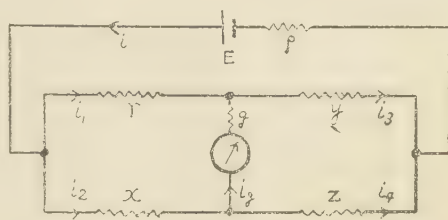


Fig. 1.  $x, y, z, r, \rho, g$  are total resistances of the path between two corresponding junctions

and we consider the values of  $x, y$  which give the least value to  $\mathcal{A}$ .

I. When  $i_1 \leq I_1, i_2 \leq I_2$

At the beginning, we consider that  $i_1, i_2$  have tolerance limits which are  $I_1, I_2$  respectively.

Let

$$\frac{E}{I_1} = R_1, \quad \frac{E}{I_2} = R_2 \dots\dots\dots (5),$$

then we have

$$R_1 - r \leq y, \quad rR_2 \leq x(y+r) \dots\dots\dots (6),$$

and we consider the least value of  $\mathcal{A}$  under the inequalities (6).

In  $(x, y)$  plane, the domain in which the co-ordinate  $(x, y)$  of a point satisfy the inequalities (6) is the shaded part in Fig. 2. and Fig. 3..

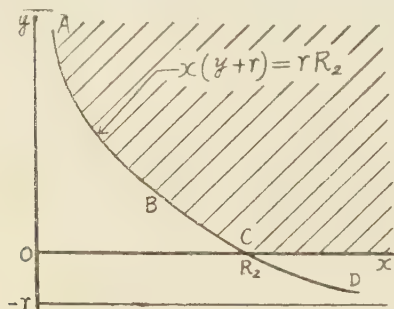


Fig. 2. Shaded part is the domain of points whose coordinates satisfy the inequality  $R_2 r \leq x(y+r)$  when  $R_1 - r \leq 0$ .

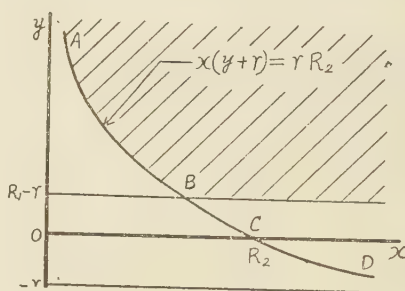


Fig. 3. Shaded part is the domain of points whose coordinates satisfy the inequality  $R_2 r \leq x(y+r)$  when  $R_1 - r > 0$ .

It is obvious that if we give a value to  $y$ , then  $\mathcal{A}$  is increasing function of  $x$ , therefore it is sufficient that we consider the least value of  $\mathcal{A}$  when  $(x, y)$  change along to the hyperbola  $\widehat{AB}$  or  $\widehat{BC}$ . In this case  $x = rR_2/(y+r)$ , and

$$\mathcal{A} = (y+r) \left\{ \frac{rR_2}{y+r} + r + g + \frac{g}{y} r \right\} = rR_2 + (y+r) \left( r + g + \frac{g}{y} r \right)$$

$$\frac{d\mathcal{A}}{dy} = r + g - \frac{gr^2}{y^2}, \quad \frac{d^2\mathcal{A}}{dy^2} = \frac{2gr^2}{y^3} > 0.$$

Therefore  $\mathcal{A}$  takes the minimum value at  $y = ar$ , where  $a = 1/g/(g+r)$  and there is not other maximum or minimum, consequently we get following results.



The largest value  $S_m$  of  $S$  is

(i) in case  $R_1 - r \leq \alpha r$

$$S_m = \frac{E}{(\sqrt{g} + \sqrt{g+r})^2 + R_2}$$

when

$$x = \frac{R_2}{1+\alpha}, \quad y = \alpha r$$

(ii) in case  $R_1 - r > \alpha r$

$$S_m = \frac{(R_1 - r) r E}{(R_1 + R_2)(R_1 - r)r + R_1^2 g}$$

when

$$x = \frac{R_2}{R_1} r, \quad y = R_1 - r$$

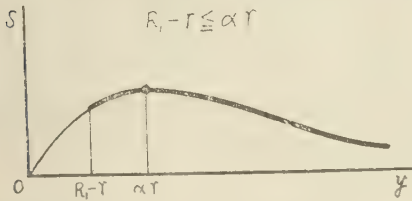


Fig. 4.

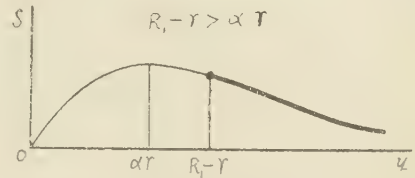


Fig. 5.

II. When  $ri_1^2 \leq w_1$ ,  $xi_2^2 \leq w_2$ ,  $yi_3^2 \leq w_3$ ,  $zi_4^2 \leq w_4$

Next, we consider that the heat quantity which is originated by current in the arms has tolerance limit, that is

$$ri_1^2 \leq w_1, \quad xi_2^2 \leq w_2, \quad yi_3^2 \leq w_3, \quad zi_4^2 \leq w_4$$

where  $w_1, w_2, w_3, w_4$  are given values. In the state of balance, putting

$$\frac{E^2}{w_n} = R_n \quad (n=1, 2, 3, 4) \quad \dots \dots \dots (7),$$

we have

$$R_1 r \leq (y+r)^2 \quad \dots \dots \dots (8),$$

$$R_2 y \leq (y+r)^2 \quad \dots \dots \dots (10),$$

$$R_2 r^2 \leq x(y+r)^2 \quad \dots \dots \dots (9),$$

$$R_1 r y \leq x(y+r)^2 \quad \dots \dots \dots (11).$$

Therefore we must consider the largest value of  $S$  under the condition that  $x, y$  satisfy these four inequalities. Graphically, in  $(x, y)$  plane, the domain in which the co-ordinates  $(x, y)$  of a point satisfy above inequalities are shaded parts in the following figures. Consequently we may seek after the largest value of  $S$  or the least value of  $J$  when  $x, y$  are the co-ordinates of a point which lays on the common part to above four cases.

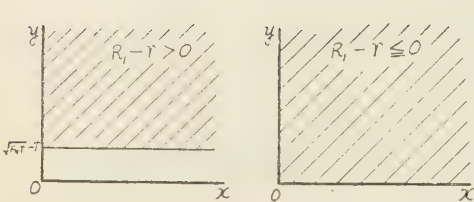


Fig. 6. when  $R_1 - r > 0$  Fig. 7. when  $R_1 - r \leq 0$   
Shaded part is the domain of points whose coordinates satisfy the inequality  $R_1 r \leq (y+r)^2$ .

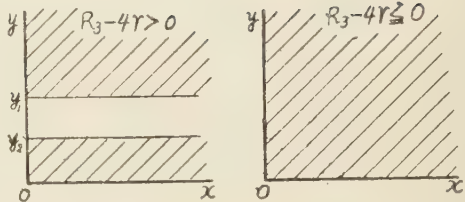


Fig. 8. when  $R_3 - 4r > 0$  Fig. 9. when  $R_3 - 4r \leq 0$   
Shaded part is the domain of points whose coordinates satisfy the inequality  $R_3 y \leq (y+r)^2$   
where  $y_1 = \frac{1}{2} \{ R_3 - 2r + \sqrt{R_3(R_3 - 4r)} \}$ ,  
 $y_2 = \frac{1}{2} \{ R_3 - 2r - \sqrt{R_3(R_3 - 4r)} \}$

In the first place, two curves

$$x(y+r)^2 = R_2 r^2 \dots\dots\dots (12), \quad x(y+r)^2 = R_4 r y \dots\dots\dots (13).$$

intersect to each other at only one point  $Q(R_2/(1+P_2)^2, P_2 r)$  and their relative positions are shown in Fig. 10., and the common region to the inequalities (9) and (11) is shaded

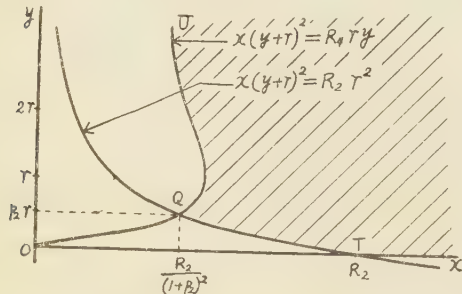


Fig. 10. Shaded part is the domain of points whose coordinates satisfy the simultaneous inequalities  $R_2 r^2 \leq x(y+r)^2$ ,  $R_4 r y \leq (y+r)^2$ .

part, where  $P_2 = R_2/R_4$ .

It is obvious that  $\Delta$  is increasing function of  $x$  when  $y$  is fixed, therefore we may seek after the least value of  $\Delta$  when  $x, y$  are the co-ordinates of a point which moves along to the curve  $UQT$  in which we should remove the parts which lay in the unshaded part in Fig. 6. .... Fig. 9..

When  $P(x, y)$  moves along to the curve (12), we have

$$x = \frac{R_2 r^2}{(y+r)^2}, \quad \Delta = \frac{R_2 r^2}{y+r} + (r+g)y + \frac{gr^2}{y} + r^2 + 2gr,$$
$$\frac{d\Delta}{dy} = r+g - \frac{R_2 r^2}{(y+r)^2} - \frac{gr^2}{y^2}, \quad \frac{d^2\Delta}{dy^2} = \frac{2R_2 r^2}{(y+r)^3} + \frac{2gr^2}{y^3} > 0,$$

therefore  $\Delta$  takes a minimum value at  $y = \beta$ , where  $\beta$  is the positive root of

$$r+g - \frac{R_2 r^2}{(\beta+r)^2} - \frac{gr^2}{\beta^2} = 0 \dots\dots\dots (14).$$

and it is easily shown that

$$\beta < r \text{ when } r > \frac{R_2}{4}$$
$$\beta = r \text{ when } r = \frac{R_2}{4}$$
$$\beta > r \text{ when } r < \frac{R_2}{4} .$$

Similarly, when  $P(x, y)$  moves along to the curve (13), we have following result.  
 $\Delta$  takes a minimum value at  $y=k$ , where  $k$  is the positive root of the equation

$$r + g + \frac{R_1 r^2}{(k+r)^2} - \frac{gr^2}{k^2} = 0 \quad (15),$$

and always  $k < r$ .

In the following, some special cases are treated.

### III. When $R_2 = R_4$

In this case, we have  $P_2 = 1$  and the intersection of (12) and (13) is  $Q\left(\frac{R_2}{4}, r\right)$ .

At first,  $\Delta$  is always in decreasing state when  $P(x, y)$  moves along to the curve (13) from  $U$  to  $Q$  because  $k < r$ . Next, when  $P(x, y)$  moves along to the curve (12) from  $Q$  to  $T$ , we have

"when  $r \leq \frac{R_2}{4}$  .....  $\Delta$  is always in increasing state because  $\beta \geq r$

when  $r > \frac{R_2}{4}$  .....  $\Delta$  takes a minimum value at  $y = \beta$  because  $\beta < r$ ."

Consequently, when  $P(x, y)$  moves along to the curve  $UQT$ , the point which gives the least value to  $\Delta$  is

"when  $r \leq \frac{R_2}{4}$  .....  $x = \frac{R_2}{4}, y = r$

when  $r > \frac{R_2}{4}$  .....  $x = \frac{R_2 r^2}{(\beta + r)^2}, y = \beta$ "

Moreover, considering the cases Fig.6. .... Fig.9., we should decide the least value of  $\Delta$  lastly.

### IV. When $r \geq R_1, \frac{1}{4} R_2, \frac{1}{4} R_3$ and $R_2 = R_4$

In this case the inequalities (8) and (9) are satisfied every value of  $x, y$  as shown in Fig.7. and Fig.9., therefore we may consider the case  $r > \frac{R_1}{4}$  in the case III. and we have the following result

$$S_m = \frac{rE}{\frac{R_2 r^2}{\beta + r} + (\beta + r) \left( r + g + \frac{g}{\beta} r \right)} \quad \text{where } r + g - \frac{R_2 r^2}{(\beta + r)^2} - \frac{gr^2}{\beta^2} = 0.$$

### V. When $R_1 = R_2 = R_3 = R_4 = R_0$

(i) when  $R_0 \leq r$

This case is included in the case IV.

(ii) when  $R_0/4 \leq r < R_0$



In this case  $\sqrt{R_0 r} - r \leq y$  must be satisfied, and we can show easily that  $\sqrt{R_0 r} - r \leq \beta$ , therefore the result coincides with the result of (i).

(iii) when  $r < R_0/4$

In this case  $y$  must satisfy

$$\sqrt{R_0 r} - r \leq y \quad \text{and} \quad \begin{cases} y_1 \leq y \\ y_2 \geq y \end{cases}$$

together as shown in Fig. 6. and Fig. 8., while we can easily show that  $y_2 < \sqrt{R_0 r} - r < y_1$  and  $r < y_1$ ,

therefore  $S$  takes the largest value when  $y = y_1$  and in this case it becomes that  $x = r$ , that is

$$S_m = \frac{rE}{(y_1 + r) \left( 2r + g + \frac{g}{y_1} r \right)}$$

when  $x = r$ ,  $y = y_1 = \frac{1}{2} \left\{ R_0 - 2r + \sqrt{R_0 (R_0 - 4r)} \right\}$ .

### 3. Some Comments

Let the deflection of a galvanometer be  $D$ , and the sensitivity  $\sigma$  of the galvanometer may be defined by

$$\sigma = \lim_{\partial i_g \rightarrow 0} \frac{\partial D}{\partial i_g} = \frac{\partial D}{\partial i_g} \quad (16),$$

and if we define the sensitivity  $S'$  of a bridge by

$$S' = \lim_{\partial r_n \rightarrow 0} \left| r_n \frac{\partial D}{\partial r_n} \right| = \left| r_n \frac{\partial D}{\partial r_n} \right| \quad (17)$$

where  $r_n$  is one of  $r$ ,  $x$ ,  $y$  and  $z$ . Then it is obvious that

$$S' = \sigma S = \frac{\sigma r E}{A} \quad (18).$$

Generally, in practice, the resistance boxes have not the required values and in such cases we are obliged to take the nearest values to them.

### References

1. Numakura: Denki-Sokutei, Butsuri Jikkengaku Vol.7. (in Japanese)
2. T. T. Smith: The Constant Battery Wheatstone Bridge, American Journal of Physics Vol. 21, No. 4. (1953)

# THE EFFECT OF THE CHANGES OF CLIMATIC ELEMENTS UPON THE NATURAL LEAK OF THE ELECTROMETER (PART I)

Keisuke KAMINISHI

(Received January 31, 1954)

## Abstract

By comparing the results of harmonic analysis of natural leak of the electrometer with those of the temperature and the relative humidity, the writer discussed the correlation between them, and reached to the following results:

the rate of the amount of natural leak caused by the variation

(1) of the temperature  $\alpha = -9.8 \times 10^{-4}$  div./min. per  $1^\circ\text{C}$

and (2) of the relative humidity  $\beta = 3.2 \times 10^{-4}$  div./min. per 1%.

Therefore it may be said that the amount of the natural leak depends chiefly upon the atmospheric temperature in the process of measurements by Mr. T. Yamamoto.

## 1. Introduction.

Formerly Mr. T. Yamamoto discussed the effect of the temperature and the relative humidity upon the natural leak [1]. He concluded that the amount of natural leak depends mainly upon the temperature and scarcely upon the relative humidity. In this paper the writer tried to check his conclusion and reached to the following results.

## 2. Harmonic Analysis of Observed Values.

Let  $L$  (div. /min.) : the reduced natural leak

$T$  (deg. Cent.) : the reduced temperature

$H$  (per cent) : the reduced relative humidity,

and express their monthly amounts in the following formula:

$$N = N_0 + N_1 \cos(t - \theta_1) + N_2 \cos(2t - \theta_2) + \dots$$

then we have the results shown in table 2 by the analysis of table 1.

Now the writer consider the annual and semi-annual variation term.

And errors are as following:

$$L = 98.1 + 91.3 \cos(t - 13^\circ) + 12.3 \cos(2t - 344^\circ) \pm 30\%$$

$$T = -12.0 + 10.9 \cos(t - 190^\circ) \pm 18\%$$

$$H = -4.7 + 5.2 \cos(t - 216^\circ) + 3.9 \cos(2t - 348^\circ) + 22\%$$

We will investigate the correlation between them by comparing the corresponding terms.

TABLE 1

## Monthly Elements

Month	Natural Leak	Temp.	Relative Humidity
(1952)	div./min.	°C	%
8	0.0684	26.8	81.7
9	0.0700	23.5	81.1
19	0.0736	16.1	74.4
11	(0.0789)	(10.2)	(76.5)
12	0.0834	6.1	78.1
(1953)			
1	0.0844	4.4	73.7
2	0.0843	6.0	71.3
3	0.0743	9.7	71.0
4	0.0789	13.4	65.3
5	0.0660	18.8	73.4
6	(0.0651)	(22.8)	(81.0)
7	0.0650	26.3	81.9
8	0.0600	28.1	78.9
Total	0.9523	212.2	988.3
Mean	0.0733	16.3	76.0

## All data reduced refer to August

Month	Natural Leak	Temp.	Relative Humidity
	$\times 10^{-4}$ div./min.	°C	%
1	195	-22.9	-6.8
2	201	-21.4	-9.0
3	108	-17.8	-9.1
4	161	-14.2	-14.5
5	39	-9.0	-6.2
6	37	-5.1	+1.6
7	43	-1.7	+2.8
8	0	-0.0	-0.0
9	23	-3.4	-0.4
10	66	-10.9	-6.8
11	126	-16.8	-5.5
12	178	-21.1	-2.6
Mean	98.1	-12.0	-4.7

TABLE 2

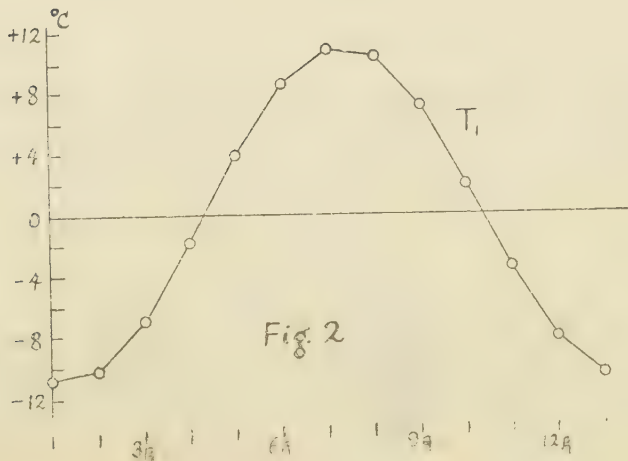
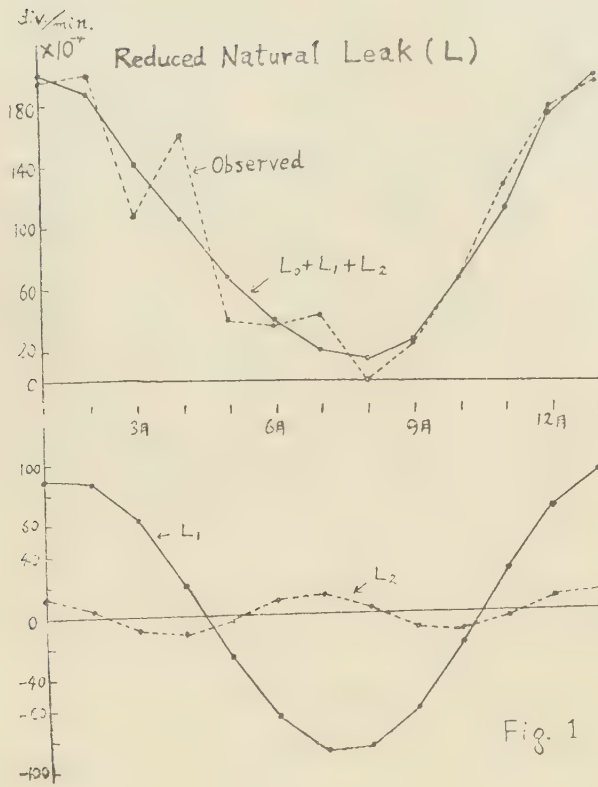
## The Results of Harmonic Analysis of Elements

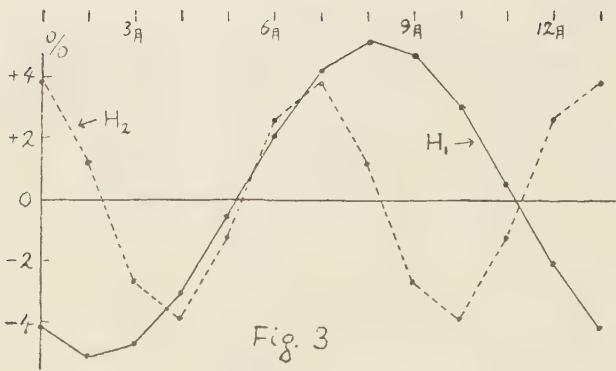
		H <sub>1</sub>	N <sub>1</sub>	$\epsilon_1$	N <sub>2</sub>	$\epsilon_2$	N <sub>3</sub>	$\epsilon_3$	N <sub>4</sub>	$\epsilon_4$	N <sub>5</sub>	$\epsilon_5$	N <sub>6</sub>	$\epsilon_6$
Natural Leak	$L \cdot 10^{-1}$	98.1	91.3	13°	12.3	344°	6.7	240°	18.4	9°	10.7	155°	9.1	180°
Temp.	T °C	12.0	10.9	190°	1.4	89°	0.39	296°	0.40	176°	0.05	202°	0.09	0°
Relative Humidity	H %	-4.7	5.2	216°	3.9	348°	0.55	119°	1.4	222°	0.50	223°	0.12	180°

1) It will be seen in the table 2 that the annual term is the most important in every element. Fig. 1, 2 show that the difference of phase angle between the annual term of the leak ( $L_1$ ) and of the temperature ( $T_1$ ) is about  $180^\circ$ , in other words the maximum and minimum of T correspond to the minimum and maximum of L respectively. On the other hand I find the discrepancy of phase angle between  $L_1$  and the annual term of the relative humidity (see Fig. 1, 3). These facts indicate that the amount of the natural leak depends chiefly upon the temperature in the process of measurements by M. T. Yamamoto.

However as  $H_1$  is pretty large, it is possible to consider that the effect of H is covered with the overwhelming effect of T. In this way it is inapt to compare the annual terms only. Then I will consider the semiannual term ( $L_2$  and  $H_2$ ). Fig. 1 and 3 show that  $L_2$  and  $H_2$  change simultaneously, besides  $H_1$  is rather large, therefore I may presume that this is the effect of H upon the L, which is not conspicuous because of being covered with







the effect of temperature. Then it is natural to assume that the ratio (the amplitude of  $L_2$ ): (the amplitude of  $H_2$ ) means the rate of  $L$  caused by  $H$ , then

$$\beta=3.2 \times 10^{-4} \text{ div./min. per } 1\%$$

2) Next for the purpose of investigating the comparatively pure effect of  $T$ , I calculate the monthly values of  $L_H=L-\beta H$  and express them as follows:

$$L_H=N_0+N_1 \cos (t-\theta_1)+N_2 \cos (2t-\theta_2)+\cdots \cdots$$

then I have the results shown in table 3. In this table I find that  $L$  (annual term) is decisively large as compared with the other terms. Moreover the difference of phase angle between  $L_H$  and  $T_1$  is about  $108^\circ$ . Therefore we regard the ratio (the amplitude of  $L_H$ ): — (the amplitude of  $T_1$ )= $\alpha$  as the rate of  $L$  caused by  $T$ , then

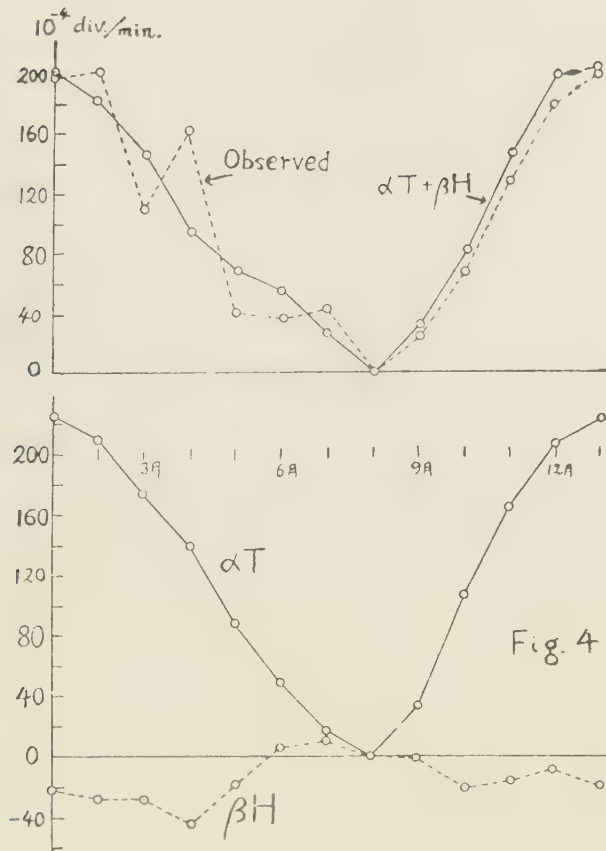
$$\alpha=-9.8 \times 10^{-4} \text{ div./min. per } 1^\circ \text{C}$$

where negative sign means that the increase of  $T$  causes the decrease of  $N$ .

3) Fig. 4 shows that the comparison of calculated values with the observed values. I can find the rather good coincidence.

TABLE 3  
The Results of Harmonic Analysis of Residuals

	$N_0$	$N_1$	$e_1$	$N_2$	$e_2$	$N_3$	$e_3$	$N_4$	$e_4$	$N_5$	$e_5$	$H_5$	$e_5$
$L_H$	113	107	13	4.3	$265^\circ$	7.6	$251^\circ$	25	$18^\circ$	24	$113^\circ$	11	$180^\circ$



### 3. Conclusions.

The main points of the present researches are summarised as follows;

- 1) The rate of the amount of natural leak caused by the variation of the temperature

$$\alpha = -9.8 \times 10^{-4} \text{ div./min. per } 1^{\circ}\text{C}$$

- 2) The corresponding value by the variation of the relative humidity

$$\beta = 3.2 \times 10^{-4} \text{ div./min. per } 1\%$$

As the amplitude of the temperature variation ( $^{\circ}\text{C}$ ) is larger than the amplitude of the relative humidity (%) and  $|\alpha| > 3\beta$ , the effect of the latter is the pretty small as compared with the former (see Fig. 4). This means that Mr. T. Yamamoto succeeded in his experiments to protect his electrometerc from the effect of the humidity.

In the next paper I should discuss

(1) the investigation of the above relations more precisely by various experiments and analysis,

(2) the study of Mr. Hatuda's relation which shows that the natural leak depends upon the temperature gradient [2].

In concluding this paper I wish to express my hearty thanks to Mr. T. Yamamoto who kindly gave me his precious data, and to Prof. Dr. M. Namba who gave me kind advices through my researches.

### References

1. T. Yamamoto: The regular meeting of Kyushu Branch of the Chemical Society of Japan  
(Des. 1953)
2. Z. Hatuda & M. Umemura:  
On the HS- fontactoscope and its application  
Shimadzu Review Vol. 8, N o. 4(1952)



# THE INVESTIGATION OF "SARA-ISI" BY THE X-RAY (Report 1)

Tadashi OKAHATA

(Received January 31, 1954)

## 1. Introduction

The rim of Sara-isi which is gathered on the volcano Aso is not a direct volcanic product, but rather a secondary one. It is made of fine particles of volcanic ashes cemented and hardened on some of the rock fragments and such like lying on the ground. Dr. M. Namba published his reserches concerning to the matter [1].

This writer intended to discriminate the upper and the lower side, mechanism of growth, and constituents of Sara-isi by taking Laue X-ray photographs.

## 2. Specimen and Experimental Procedure

A number of fragments were cut from a marginal part of a Sara-isi and they were polished about 0.3 mm. in thickness. For these speimen applied Laue method. For the apparatus of X-ray, the C+type tube of Shimadzu manufacture was used, and its target was copper. The distance between the specimen and the photographic film was held about 3 cm. The film was always set perpendicular to the incident beam of X-ray. When needed necessary, photographs were taken at some parts of a specimen.

By the way, D-S. photographs were taken with coagulated part of a Sara-isi, volcanic ashes gathered in the neighbourhood of the crater of the volcano Aso, and mud which was gathered when Kumamoto suffered a great damage by the flood on 26th. June in 1953, respectively. These photographs were taken with the same camera as before.

## 3. Experimental Results

By the experimental procedure stated above, the following results were obtained. Some of the radiographs taken with specimen which had been cut off from the rim, (specimen A and A' in Fig. 5) and the stalactitic form process of the Sara-isi (specimen B and B' in Fig. 5) are reproduced in Figs. 1, 2, 3, and 4 Plate I. Fig. 1 and 2 are radiographs with rim and Fig. 3 and 4 are with stalactitic process. In these figures we see some D-S. rings and arenaceous spots, and many spots with the rim compared with the process.

Figs. 6, 7, 8, 9 and 10 Plate II are radiographs with the specimen which had been cut off from the upper side of another Sara-isi and Fig. 11, 12, 13, 14 and 15 Plate II are radiographs with specimen from the rim of it. In these figures, we can see rings and spots same

as before, too, but in this case, they are more sharp in the latter than the former.

Thus it is ascertained that the marginal part of Sara-isi is made of micro-crystals and comparatively large crystalline grains of different kind, and they are arranged quite irregularly. Therefore, the marginal part of Sara-isi has no crystallographic structure as a fibrous arrangement.

Number of grains are large in the upper side, and small at the process in the lower side, and size of grains are finer as to come at the lower side of Sara-isi. For these reasons, it can discriminate between the upper and the lower side of a Sara-isi.

But, he can not yet ascertain by his experiment which has performed up to present, that the D-S. rings and spots in the radiographs correspond to what substances, and to what crystal systems. These will be reported in the following paper.

The radiograph which is reproduced in Fig. 16 is the one with the powdered coagulated part of Sara-isi, Fig. 17 is with the volcanic ashes, and Fig. 18 is with the mud which was gathered after the flood. About them will be discussed in the following paper, too.

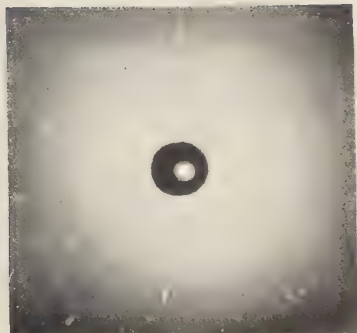
The writer wishes to express his sincere thanks to Dr. M. Namba under whose kind guidance this experiment was carried out.

### Reference

1. M. Namba: Characteristics of Activity and the Peculiar Product "Sara-Isi" of the Aso Volcano, Mem. Col. Sci. Kyoto Imp. Uni. Vol. XIX, No.3 (1936).

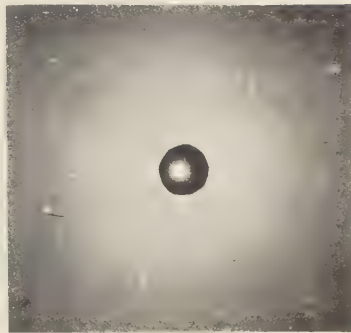
Plate I

Fig. 1



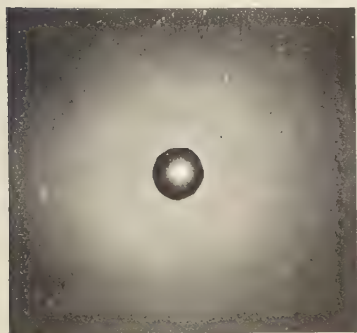
A

Fig. 2



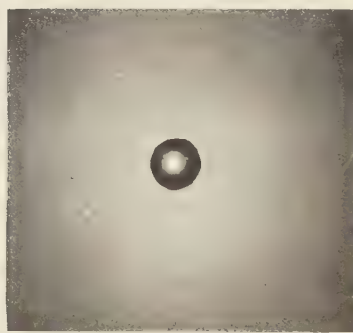
A'

Fig. 3



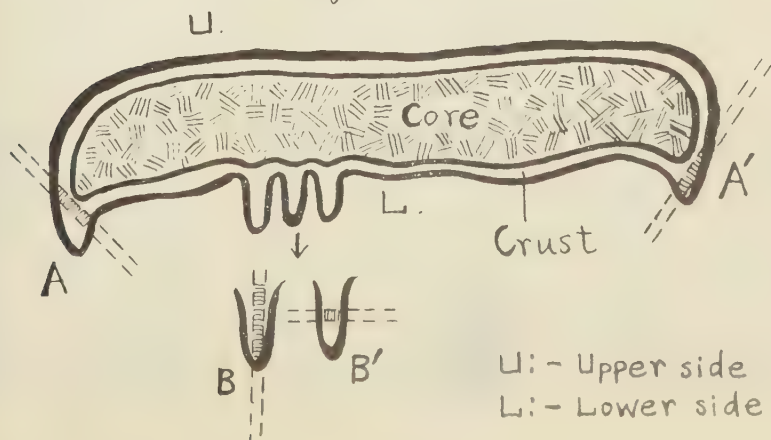
B

Fig. 4



B'

Fig. 5



U: - Upper side  
L: - Lower side

Plate II

Fig. 6

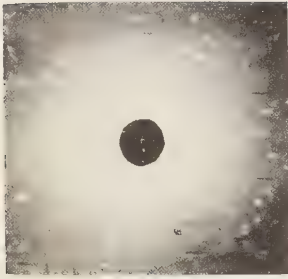


Fig. 7

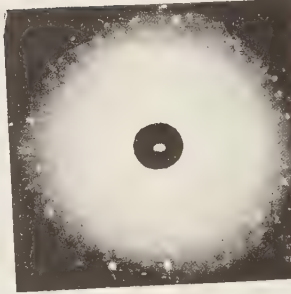


Fig. 8

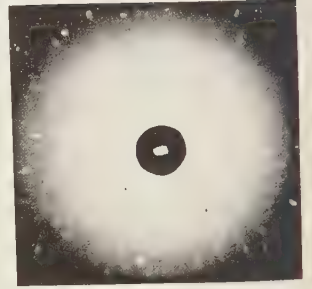


Fig. 9

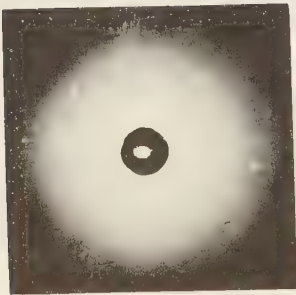


Fig. 10

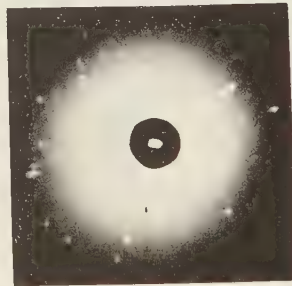


Fig. 11

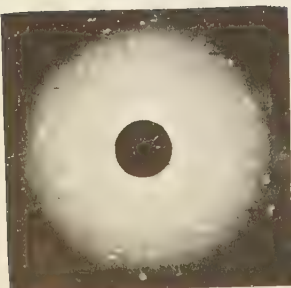


Fig. 12

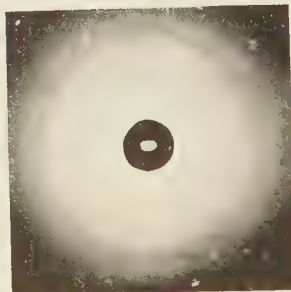


Fig. 13

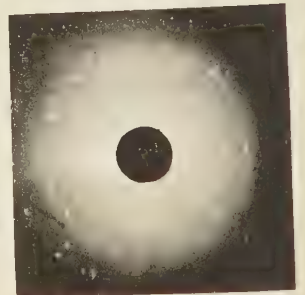




Fig. 14

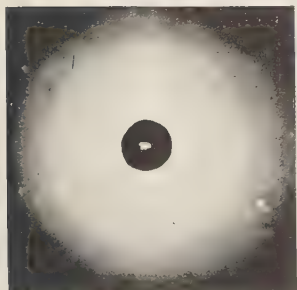


Fig. 15

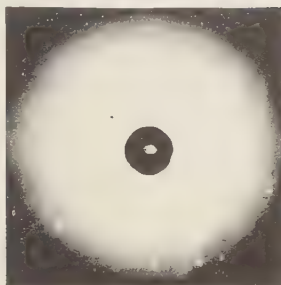


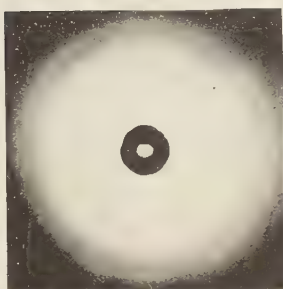
Plate III

Fig. 16



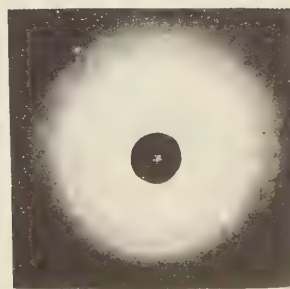
Sara-isi

Fig. 17



Volcanic ashes

Fig. 18



mud

# ON THE NUMERICAL SOLUTION OF THE SIMULTANEOUS DIFFERENTIAL EQUATIONS UNDER SOME CONDITIONS (Part 1)

Ryuzo ADACHI

## 1. Introduction

Let  $u_1(x)$ ,  $u_2(x)$ ,  $u_3(x)$  be unknown functions of  $x$  and  $F_j(x, u_1, u_2, u_3)$  be known functions of  $x, u_1, u_2, u_3$ . We take following simultaneous differential equations

$$\frac{du_j}{dx} = F_j(x, u_1, u_2, u_3), \quad j=1, 2, 3 \quad (1),$$

and consider the numerical solution of these equations under following conditions

“ on  $(x, u)$  plane, let  $X_j$  be the  $x$  coordinate of the intersection of

the solution curve  $u=u_i(x)$  and a given curve  $\Psi_j(x, u)=0$  and

$$g_j\{X_j, u_1(X_j), u_2(X_j), u_3(X_j)\} = 0 \quad (2)$$

must be satisfied, where  $i=\text{one of } 1, 2, 3$  and  $j=1, 2, 3$  and  $g_j$  are given functions of  $x, u_1, u_2, u_3$ .

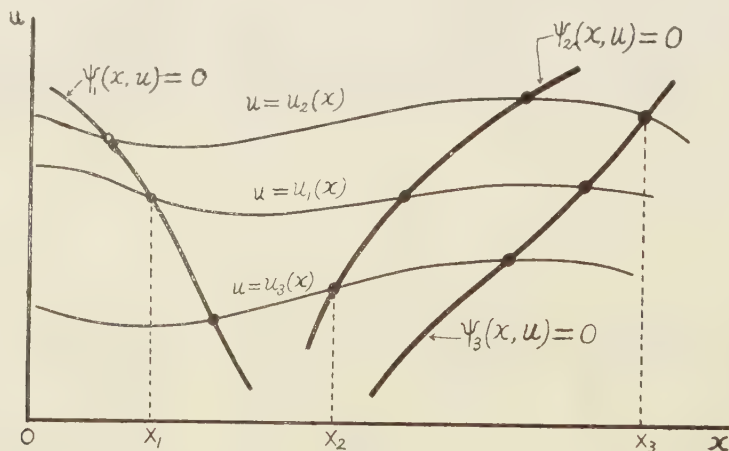


Fig. 1

## 2. Iterative method

When we employ iterative method, starting from any functions  $u_{j1}(x)$ , let  $u_{jn}(x)$  be the  $n^{\text{th}}$  approximation of  $u_j(x)$  and put

$$F_j \left\{ x, u_{1,n-1}(x), u_{2,n-1}(x), u_{3,n-1}(x) \right\} = f_{j,n-1}(x), p_{j,n}(x) = \int_{x_0}^x f_{j,n-1}(x) dx \dots\dots (3),$$

$$\text{and } \frac{du_{j,n}}{dx} = f_{j,n-1}(x) \text{ then } u_{j,n}(x) = p_{j,n}(x) + b_{j,n} \dots\dots\dots (4),$$

where  $b_{j,n}$  are indeterminate constants.

We divide the interval of  $x$  into small intervals and if we know the values of  $u_{j,n-1}(x)$  at each dividing point of  $x$ , it is obvious that the values of  $p_{j,n}(x)$  at each dividing point of  $x$  can be calculated by ordinary method, therefore our problem is how to determine the values of  $b_{j,n}$ . Let  ${}_nX_j$  be the  $x$  coordinate of the intersection of the given curve  $\phi_j(x, u) = 0$  and the  $n^{th}$  approximate solution curve  $u = u_{i,n}(x)$ , then we have following relations

$$\left. \begin{aligned} \phi_1 \{ {}_nX_1, p_{1,n}({}_nX_1) + b_{1,n} \} &= 0, \mathcal{G}_1 \{ {}_nX_1, p_{1,n}({}_nX_1) + b_{1,n}, p_{2,n}({}_nX_1) + b_{2,n}, p_{3,n}({}_nX_1) + b_{3,n} \} = 0 \\ \phi_2 \{ {}_nX_2, p_{2,n}({}_nX_2) + b_{2,n} \} &= 0, \mathcal{G}_2 \{ {}_nX_2, p_{1,n}({}_nX_2) + b_{1,n}, p_{2,n}({}_nX_2) + b_{2,n}, p_{3,n}({}_nX_2) + b_{3,n} \} = 0 \\ \phi_3 \{ {}_nX_3, p_{3,n}({}_nX_3) + b_{3,n} \} &= 0, \mathcal{G}_3 \{ {}_nX_3, p_{1,n}({}_nX_3) + b_{1,n}, p_{2,n}({}_nX_3) + b_{2,n}, p_{3,n}({}_nX_3) + b_{3,n} \} = 0 \end{aligned} \right\} \dots\dots (5).$$

$i, j, k = \text{one of } 1, 2, 3$

Solving these six equations simultaneously with respect to  ${}_nX_1, {}_nX_2, {}_nX_3, b_{1,n}, b_{2,n}, b_{3,n}$  we can determine the values of  $b_{1,n}, b_{2,n}, b_{3,n}$ .

### 3. Simplification of the conditions

Generally it is very difficult that we solve above simultaneous equations, but it is rather easy when we divide the given conditions into elementary cases. For example, it is easily shown that the condition

“on  $(x, u)$  plane, when  $X_j$  is the  $x$  coordinate of the intersection of the solution curve  $u = u_1(x)$  and a given curve  $\phi_j(x, u) = 0$ , the condition

$$\mathcal{G}_j \{ X_j, u_1(X_j), u_2(X_j), u_3(X_j) \} = 0$$

must be satisfied, where  $\mathcal{G}_j(x, u_1, u_2, u_3)$  are given functions of  $x, u_1, u_2, u_3$ ”  
can be reduced to one of the following conditions

“ (i)  $u_1(a_j) = A_j$

(ii)  $u_2(a_j) = K_j \{ u_1(a_j) \}$

(iii)  $u_3(a_j) = H_j \{ u_1(a_j), u_2(a_j) \}$

(iv)  $u_2(X_j) = K_j(X_j) \dots\dots$  at the intersection  $(X_j, U_j)$  of the solution curve  $u = u_1(x)$

and a given curve  $u = \phi_j(x)$



(v)  $u_2(X_j) = H_j\{X_j, u_1(X_j)\}$  ..... at the intersection  $(X_j, U_j)$  of the solution curve  $u = u_1(x)$  and a given curve  $u = \varphi_j(x)$

where  $a_j, A_j$  are given constants and  $K_j, H_j$  are given functions and each case can be treated considerably easily.

In the formulas (5)  $i, j, k$  can take one of 1, 2, 3 and in each case the condition can be divided into five cases as above, and even if we except similar forms there exist great number of cases.

In the next journal I will treat some typical cases which appear in physical and engineering problems, and the convergency of the solutions will be discussed.

It is easily shown that our discussion can be extended to many dimensional simultaneous differential equations.

### References

1. R. Adachi: On the numerical solution of the second order differential equations under some conditions. Kumamoto Jour. Sc. Vol.1, No.3 (1954)

## CRITICISM ON THE EXPRESSIONS OF THE SECOND LAW OF THERMODYNAMICS

Shigeichi FUJITA

### Abstract

An expression for the second law of thermodynamics is given, and on the point of view of that expression, the expressions which are seen in some text-books are criticised. These expressions, if no more detailed explanation is given, would lead the readers to any confusion or misunderstanding.

### 1. Introduction

When the system in an equilibrium state changes to another equilibrium state by some external action, the changes of entropy, internal energy, enthalpy and free energy of the system are to be definitely given if the changes of all the independent state variables are given. In some well-known text-books, however, there will be seen sometimes the expression of the second law of thermodynamics which expresses the relation between the change of a state function and the changes of the state variables by an unequal sign.

The heat absorbed and the external work done by the system are not definitely determined by the changes only of the system, since the heat and the work depend on the courses of the changes of the system. It is sometimes necessary, therefore, to use inequalities to express the relations between the heat or work and the changes of the state variables or state functions. But the relations between the changes of independent state variables and the changes of state functions are to be expressed by the equalities, i. e., the changes of state functions can be definitely determined by the changes of all the independent variables. When the expression, which states the relation between the changes of state variables and a state function only and does not contain heat or work, is given by an inequality, though it may not be erroneous, it may lead the readers to any misunderstanding.

### 2. An Expression of the Second Law of Thermodynamics

To acquire the foundation of criticism, the second law of thermodynamics is expressed in the following form.

In the equilibrium system, uniform in pressure  $p$  and temperature  $T$ , the extensive quantities  $S$  (entropy),  $V$  (volume) and  $x_1, x_2, \dots, x_n$  are given as the independent state variables. The system suffers a small change in which the changes of the independent variables are given by  $dS, dV, dx_1, \dots, dx_n$ , and absorbs a small heat  $\delta Q$  and does a small external work  $\delta W$ . Then, by the first and the second laws of thermodynamics, we obtain

$$\delta Q = dU + \delta W \quad (1)$$

$$\delta Q \leq TdS = dU + p dV + \sum_{i=1}^n X_i dx_i \quad (2)$$

where  $U$  is the internal energy of the system and  $X_i$  is the intensive variable corresponding to  $x_i$ . Separating the work  $\delta W$  into two parts, the work done by pressure  $\delta W_1$  and the work done by the forces other than pressure  $\delta W_2$ , and connecting (1) and (2), we obtain

$$dU = \delta Q - \delta W_1 - \delta W_2 = TdS - p dV - \sum_{i=1}^n X_i dx_i \quad (3)$$

and

$$dU \leq TdS - p dV - \delta W_2 \leq TdS - \delta W_1 - \delta W_2 \quad (4)$$

using the relations

$$TdS \geq \delta Q, \quad p dV \geq \delta W_1, \quad \sum_{i=1}^n X_i dx_i \geq \delta W_2 \quad (5)$$

Besides, since  $dU$  is a perfect differential, there are relations

$$T = \left( \frac{\partial U}{\partial S} \right)_{V, x_i}, \quad -p = \left( \frac{\partial U}{\partial V} \right)_{S, x_i}, \quad -X_i = \left( \frac{\partial U}{\partial x_i} \right)_{S, V, x_j (j \neq i)} \quad (6)$$

and  $dU$  is to be perfectly determined by the changes of all the independent state variables, i. e., the relation between  $dU$  and the changes of all independent state variables is expressed by an equality. But to express the relations between  $dU$  and  $\delta Q$  or  $\delta W$  ( $\delta W_1$  and  $\delta W_2$ ), it is necessary to use inequalities.

When we express the first and the second laws of thermodynamics in the form of (3) and (4), we can perceive clearly the causes of the changes of entropy, enthalpy, and free energy produced by the change of the system. We shall consider some special cases in the following.

### 3. Several Special cases

#### (i) Adiabatic change

In this case  $\delta Q = 0$ , and  $\delta S \geq 0$ .

From (3) we obtain

$$TdS = (p dV - \delta W_1) + \left( \sum_{i=1}^n X_i dx_i - \delta W_2 \right) \quad (7)$$

In this form, we know that  $dS > 0$  is caused from the relations  $p dV > \delta W_1$  and  $\sum_{i=1}^n X_i dx_i > \delta W_2$ , i. e., from the irreversible changes of  $V$  and  $x_i$ .

In reversible changes,  $p dV = \delta W_1$ ,  $\sum_{i=1}^n X_i dx_i = \delta W_2$  and  $dS = 0$  hold.

#### (ii) Changes in which external work is zero

In this case  $\delta W=0$ , then from (3) we obtain

$$dU - \delta Q = TdS - pdV - \sum_{i=1}^n X_i dx_i \quad (8)$$

When this is transformed in the form

$$dS = \frac{\delta Q}{T} + \frac{pdV + \sum_{i=1}^n X_i dx_i}{T}, \quad pdV + \sum_{i=1}^n X_i dx_i > 0 \quad (9)$$

we know that  $dS > \frac{\delta Q}{T}$  is caused from the irreversible changes of  $V$  and  $x_i$  without doing work. Accordingly, if  $V$  and  $x_i$  is kept constant, though the absorption of heat is irreversible, the equality  $dS = \frac{\delta Q}{T}$  always holds.

(iii) Isothermal changes

In this case, if we use the Helmholtz's free energy  $F=U-TS$ , we obtain from (3) and (4) the following expression

$$dF = -pdV - \sum_{i=1}^n X_i dx_i \leq -pdV - \delta W_2 \leq -\delta W \quad (10)$$

The increase in  $F$  is equal to the work done reversibly and is smaller than the work done irreversibly by the outside.

If  $\delta W_2=0$ , from (10) we obtain an inequality

$$dF \leq -pdV \quad (11)$$

But this means really

$$dF = -pdV - \sum_{i=1}^n X_i dx_i, \quad \sum_{i=1}^n X_i dx_i \geq 0 \quad (12)$$

and (11) is looked as the simplified form of (12). If, therefore,  $\sum_{i=1}^n X_i dx_i = 0$  is satisfied,  $dF = -pdV$  holds even when any irreversible volume change is produced. As the inequality of (11) is caused from  $\sum_{i=1}^n X_i dx_i > 0$ , in the simple system which has only two independent variables,  $S$  and  $V$  for example, the relation  $dF = -pdV$  is always satisfied under the condition  $T=\text{const.}$ , even when any irreversible change is produced. There are, however, some textbooks which express that the relation  $dF = -pdV$  is satisfied only in the reversible volume change, and the relation  $dF < -pdV$  is satisfied in the irreversible volume change.

(iv) Isothermal-isochoric changes

In this case, from (10) we obtain



$$dF = - \sum_{i=1}^n X_i dx_i \leq -\delta W_2 \quad (13)$$

If, therefore,  $\delta W_2=0$  is satisfied, it becomes  $dF \leq 0$  which is caused from the relation  $\sum_{i=1}^n X_i dx_i \geq 0$ . The inequality comes from the fact that  $x_i$  changes without doing any work. Of course, in a simple system which has only two independent state variables, any change of state can not occur under the condition of  $T=\text{const.}$  and  $V=\text{const.}$

(v) Isobaric changes

In this case, if we use enthalpy  $H=U+pV$ , we obtain from (3) and (4)

$$dH = TdS - \sum_{i=1}^n X_i dx_i \leq TdS - \delta W_2 \quad (14)$$

In the case of  $\delta W_2=0$ , we obtain an inequality  $dH \leq TdS$  which is to be seen as a simpler form of the expression

$$dH = TdS - \sum_{i=1}^n X_i dx_i, \quad \sum_{i=1}^n X_i dx_i \geq 0 \quad (15)$$

As the inequality causes from the term  $\sum_{i=1}^n X_i dx_i$ , if the condition  $\sum_{i=1}^n X_i dx_i = 0$  is satisfied,  $dH = TdS$  holds always even though the change is reversible or irreversible under the condition  $p=\text{const.}$  Accordingly, in a simple system which has only two independent variables, the equality  $dH = TdS$  holds always even if any irreversible change would occur under the condition  $p=\text{const.}$

(vi) Isothermal-isobaric changes

In this case, if we use the Gibbs' free energy  $\Phi = U - TS + pV = F + pV = H - TS$ , we obtain from (3) and (4)

$$d\Phi = - \sum_{i=1}^n X_i dx_i \leq -\delta W_2 \quad (16)$$

The increase of the Gibbs' free energy is smaller than the work done irreversibly and is equal to the work done reversibly by the forces other than pressure from outside.

When  $\delta W_2=0$ , (16) becomes

$$d\Phi = - \sum_{i=1}^n X_i dx_i \leq 0 \quad (17)$$

From this we know that the change, capable under the condition  $\delta W_2=0$ , is only in the direction of  $\sum_{i=1}^n X_i dx_i \geq 0$  or  $d\Phi \leq 0$ .

If  $\sum_{i=1}^n X_i dx_i = 0$ , it becomes  $d\Phi = 0$ , i. e., the Gibbs' free energy do not change even when

any irreversible change will occur under the conditions  $T=\text{const.}$  and  $p=\text{const.}$  Of course, the simple system which has only two independent state variables can not change its state under the conditions  $T=\text{const.}$  and  $p=\text{const.}$  There are, however, some text-books whose explanations would lead the readers to any misunderstanding as if the Gibbs' free energy of a simple system which has only two independent variables would vary in the case of any irreversible change under the conditions  $T=\text{const.}$  and  $p=\text{const.}$

As the situation is different, either the number of independent variables is two or more than two, either the work done by forces other than pressure comes in consideration or not, it is necessary to show at first what changes of system we treat. If it were not clearly showed at first, the readers would be lead to any confusion or misunderstanding.

Thus the changes of entropy, internal energy, enthalpy, Helmholtz's free energy and Gibbs' free energy by the changes of state of a system are given definitely by the changes of all the independent state variables, in the form of equalities.

It may be used inequalities when the changes of a part of independent variables are not clearly known, or when it is not necessary to know exactly the changes of state. But it becomes sometimes necessary to use inequalities when we would express the relations between the changes of the state functions or the variables of the system and the heat absorbed or the work done by the system.

In the following, on the foundation of this point of view, we shall criticise the expressions of the second law of thermodynamics which are seen in some well-known text-books.

#### 4. Criticism on the Expressions of the Second Law of Thermodynamics

(i) On the page 22 of the text-book [1], we see the following sentence and expressions

"Instead of using volume and temperature as independent variables, however, we more often wish to use pressure and temperature. In this case, instead of using the Helmholtz free energy, it is more convenient to use the Gibbs free energy  $G$ , defined by the expressions

$$\begin{aligned} G &= H - TS = U + PV - TS = A + PV \\ dG &= dH - TdS - SdT = dU + PdV + VdP - TdS - SdT \end{aligned} \quad (3.8)$$

By equation (1), this is

$$dG \leq VdP - SdT \quad (3.9)$$

(Note: equation (1) means  $dW \leq TdS - dU$ )

For a system at constant pressure and temperature, we see that the Gibbs free energy is constant for a reversible process but decreases for an irreversible process, reaching a minimum value consistent with the pressure and temperature for the equilibrium state."

The inequality (3.9) is doubtful. It is stated in the book that (3.9) is obtained by putting (1) in (3.8). But we obtain the following expression, different from (3.9), by putting practically (1) in (3.8)

$$dG \leq VdP - SdT + PdV - dW$$

It is considered that this inequality occurs from the relation  $PdV \geq dW$  and the equation  $dG = VdP - SdT$  holds always in the given case. It is, therefore, considered that under the conditions  $T = \text{const.}$  and  $P = \text{const.}$ ,  $G$  is also constant ( $dG = 0$ ). The system treated here has only two independent variables, and therefore, under the given conditions, any change must not be produced in the system.

(ii) On the page 428 of the text-book [2], we see the following sentence and expressions.

" 3. Isothermal Process. — Here  $T$  remains constant and therefore (3) can be written in the form

$$(\text{Note: (3) means } dU - TdS \leq -dW)$$

$$d(U - TS) \leq -dW$$

Let us define a function  $F = U - TS$ . Then

$$dF \leq -dW \tag{5}$$

.....

4. Isothermal-Isochoric Reactions. — If in addition there is no change in volume, the external work done is zero, and hence

$$dF \leq 0 \tag{6} "$$

In the case treated here, the work is only one done by pressure and the other works are out of consideration. Then it is considered that (5) means

$$dF = -pdV \leq -dW$$

In the case of isothermal-isochoric change, it can not be said that since  $dW = 0$ , we obtain (6). It is to be said that since  $V$  is const.,  $dW = 0$  and  $pdV = 0$  hold at the same time, and we obtain, instead of (6)  $dF = 0$ .

It is clearly supposed that the system treated here has two independent variables by the following sentence written in the page 429 of the book.

" From the definition of  $F$ , viz.,  $F = U - TS$  we have  $dF = -pdV - SdT$  "

Also on the page 433 of the book we see the following sentence and expressions

“ 7. Isothermal-Isobaric Process

When both the temperature and pressure remain constant and the external work done is due to change in volume,  $dW = p dV$  and the condition for an isothermal case

$$dF \leq -dW$$

becomes

$$dF \leq -p dV$$

or

$$d(U - TS + pV) \leq 0$$

The function  $\phi = U - TS + pV$  is known as the thermodynamic potential. Hence the condition of change is  $d\phi \leq 0$ .

Further from definition of  $\phi$  we observe that

$$d\phi = V dp - S dT \quad "$$

In the change under the conditions  $T = \text{const.}$  and  $p = \text{const.}$ , the relation  $dW \leq p dV$  is to hold also, and therefore from the relation  $dF = -p dV \leq -dW$  we obtain  $d(F + pV) = d\phi = 0$ .

It is clearly supposed that the system treated here has only two independent variables, if we observe the last expression  $d\phi = V dp - S dT$ . From this equation also, we see clearly that  $d\phi = 0$  under the conditions  $T = \text{const.}$  and  $p = \text{const.}$

In the system, having only two independent variables, any change could not be produced under the conditions  $T = \text{const.}$  and  $p = \text{const.}$

(iii) On the page 434 of the text-book [3], we see the following sentence and expressions.

“ Wenn wir in der Definitionsgleichung der Entropie für  $dQ_o(\text{rev})$  gemäß dem ersten Hauptsatz  $du + p dV$  schreiben, erhalten wir in der differentieller Form aus (19)

$$\left( \text{Note: (19) means } S = \int \frac{dQ_o(\text{rev})}{T} \right)$$

$$(22) \quad dS = \frac{dU + p dV}{T}$$

.....

Wenn wir ein und dasselbe System von einem in den anderen Zustand bringen, so muß diese Änderung reversibel geleitet werden, wenn die Gleichung (22) bestehen soll. Bei einer irreversiblen Zustandsänderung ist dagegen, wenn wir (21) in differentieller Form schreiben und wieder den 1. Hauptsatz anwenden,

$$(23) \quad \delta S - \frac{\delta U + p\delta V}{T} > 0$$

$$\left( \text{Note: (21) means } S_2 - S_1 > \int_1^2 \frac{dQ_o(irr)}{T} \right) \quad "$$

As the expressions (22) and (23) contain state variables only and do not contain heat or work, it is questionable that (23) has an unequal sign. It is considered that the relation  $dQ_o(rev) = dU + p dV$  holds by reversible change and the relation  $dQ_o(irr) < dU + p dV$  holds by irreversible change. Hence, instead of the expressions (22) and (23), we must use

$$(22') \quad dS = \frac{dU + p dV}{T} = \frac{dQ_o(rev)}{T}$$

$$(23') \quad dS = \frac{dU + p dV}{T} > \frac{dQ_o(irr)}{T}$$

Also at the lower part of the same page, we see the following sentence and expression

" Bei einer irreversiblen, von selbst verlaufenden Zustandsänderung gibt stets die Ungleichung (23). Sie läßt sich im vorliegenden Fall wegen der vorausgesetzten Konstanz von  $T$  und  $V$  schreiben

$$(25) \quad \delta(U - TS) = \delta F < 0 \quad "$$

It is considered that by (23') the following expression (25') holds instead of (25)

$$(25') \quad d(U - TS) = dF = 0$$

On the page 435, we see the following sentence and an expression

" Ebenso verfahren wir mit einem System, das unter konstanter Temperatur und konstantem Druck gehalten wird (dies ist die wichtigste Nebenbedingung). Wir erhalten aus (23) bei konstantem  $p$  und  $T$  für eine irreversible Zustandsänderung

$$(28) \quad \delta(U - TS + pV) = dG < 0 \quad "$$

It is considered that by (23') the expression  $d(U - TS + pV) = dG = 0$  holds instead of (28). Under that sentence, we see the following sentence and expression

" Für ein isentropisch-isobares System folgt aus (23) bei konstantem  $S$  und  $p$



$$(30) \quad \delta(U+pV) < 0 \quad "$$

It is considered that by (23') also the expression  $d(U+pV)=0$  holds instead of (30).

On the above we have given few examples stated in the well-known text-books. We see some more examples of text-books which employ ambiguous expressions that may lead the readers to any confusion or misunderstanding.

### Literature

- [1] J. C. Slater : Introduction to Chemical Physics (1989)
- [2] M. N. Saha & B. N. Srivastava : A Text Book of Heat (1981)
- [3] G. Joos : Lehrbuch der Theoretischen Physik (1982)

# THE EFFECT OF THE HEAT-TREATMENT ON THE LONGITUDINAL MAGNETOSTRICTION IN WEAK MAGNETIC FIELD

Sigeo MATSUMAE

## (1) Introduction.

As the longitudinal magnetostriction in the weak magnetic field, in which the permeability is constant, is observed in nickel and is greatly affected by the internal stress in the specimen, we take measurement of the effect of the heat-treatment on the longitudinal magnetostriction in the initial permeability range.

According to the results of the experiments, the longitudinal magnetostriction in weak magnetic field is greatly affected by the heat-treatment. The experimental results are as follows.

## (2) Experimental results and Discussion.

Experimental apparatus and method of measurement are the same as described in the previous paper.<sup>(1)</sup> As shown in Fig. 1, the left hand side of the specimen is magnetized by the alternating-current supplied by the beat-oscillator but, on the other hand,

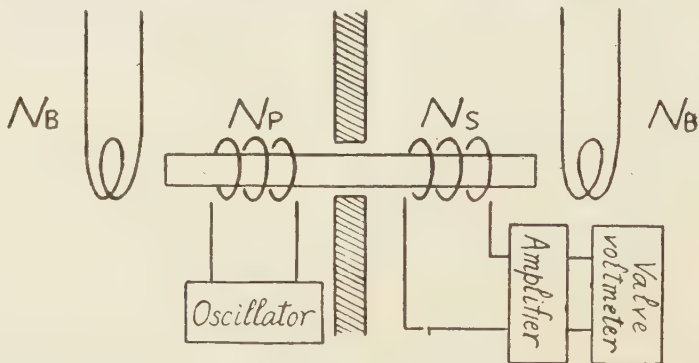


Fig. 1.

the right hand side of the specimen is left unmagnetized as the result of shielding. When the frequency of the alternating-current approaches the lengthwise mechanical resonance-frequency of the specimen, the right hand side of the specimen begins to vibrate longitudinally and vibrates most intensely at the same frequency as that of the lengthwise mechanical resonance of specimen. As the result of the Villari-effect, the electric voltage is induced in the secondary coil  $N_S$ , that is proportional to the longitudinal magnetostriction. The induced voltage is amplified by the audio-frequency amplifier and then measur-

ed by the valve-volt-meter.

The specimen is a round bar of the electrolytic nickel, containing about 0.3% manganese, 58 cm in length and 6 cm in diameter.

Considering the fact that the longitudinal magnetostriction in the initial permeability range is so greatly affected by the method of demagnetization, by demagnetizing the specimen by an alternate magnetic field or by heating which means demagnetizing the specimen in such a manner that the specimen is horizontally set in an electric furnace in the direction east to west, making the axis of the specimen perpendicular to the earth-magnetic field and heated above the critical temperature and then cooled to the room temperature without the existence of the magnetic field produced by the heating current, we take measurement of the longitudinal magnetostriction in the initial permeability range in the condition demagnetized by heating.

Before each heat-treatment, the same specimen is cold-worked, and the condition of the internal stress in the specimen generated by the cold-work is, exactly speaking, not same in each case.

After the cold-work, the specimen is set in the electric furnace, heated from the room temperature to 800°C in about 40 minutes by flowing the constant electric current through the heating-wire of the electric furnace, and then hold at the same temperature in the course of four different times, 5, 10, 20, 60 minutes, finally being cooled to the room-temperature with the electric-furnace by cutting the heating-current off. Of course, the rate of cooling varies somewhat with the duration of annealing.

Fig. 2 shows the relation between the duration of the annealing and the magnitude of the scale-readings of the valve-voltmeter. Naturally, the magnitudes of the longitudinal magnetostriction are proportional to the electric voltages induced in the secondary coil but the proportional constants are not same in each case. In consequence of the fact, the scale-readings of the valve-voltmeter do not exactly denote the magnitudes of the longitudinal magnetostriction in each case. But, as the variations of the proportional constants are comparatively small, the rough tendency may be obtained in the measurements of the scale-readings of the valve-voltmeter.

The initial permeability of the specimen is ballistically measured and, according to the results of the measurements, the magnitudes of the initial permeability are somewhat different even in the case of the same heat-treatment and, on an average, has a tendency to increase with the increase of the duration of annealing.

On the contrary, the magnitudes of the scale-readings of the valve-voltmeter in the initial permeability range is not simple as the initial permeability. As shown in Fig. 2, the magnitude of the induced voltage shows a large variation even in the case of the same heat-treatment, that seems to be caused chiefly by the difference of the condition of the internal stress in the specimen which is generated by the cold work, as above mentioned, and by the difference of the conditions of magnetic domains in the specimen, and shows, on an average, a tendency to increase at the origin with the increase of the duration

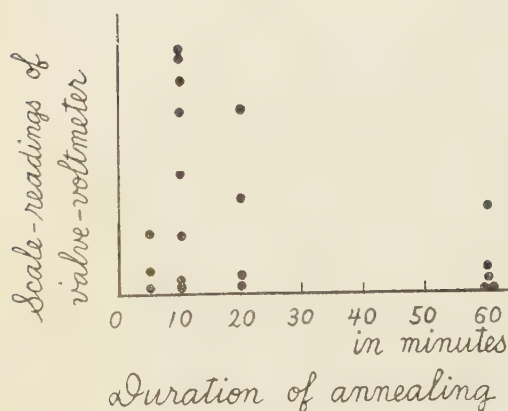


Fig. 2.

ture of 900°C. And, at the lower temperature than 800°C, the same tendency as at 800°C is also observed but the width of the peak becomes broader gradually.

In the permivar-alloy which has the long range of the initial permeability, the longitudinal magnetostriction is also observed in the initial permeability range.<sup>(2)</sup> Further, the longitudinal magnetostriction in the initial permeability range is greatly affected by the heat-treatment, namely by the annealing-temperature and the duration of annealing, and, on the whole, the same tendency as in the case of nickel is also observed.

### (3) Summary.

According to the results of the measurements, the longitudinal magnetostriction in the weak magnetic field, in which the permeability is constant, is observed in nickel and also permivar-alloy which has the long range of the initial permeability. It is greatly affected by the heat-treatment and, on the whole, this seems to be chiefly caused by the condition of the internal stress in the specimen.

### References.

- (1) S. Matsumae : Sci. Rep. of TOHOKU-university. XXXI. IV.
- (2) S. Matsumae : KUMAMOTO Journal of Science. 1. 1.

# SOME STUDIES ON VOLCANO ASO AND KUJIU (PART 9) THE FLOOD OF THE RIVER SHIRAKAWA ON JUNE 26-27, 1953

(THE 1st REPORT)

Tosisato. MUROTA

Received January 31, 1954)

## Abstract

This is a study on the flood of the River Shirakawa which took place on June 26-27, 1953. In this paper, the writer treats the time when the highest water level appeared along the River Shirakawa which is running through Kumamoto Prefecture from east to west, and he discusses the relation between the rainfall in the catchment basin and the flood in Kumamoto City.

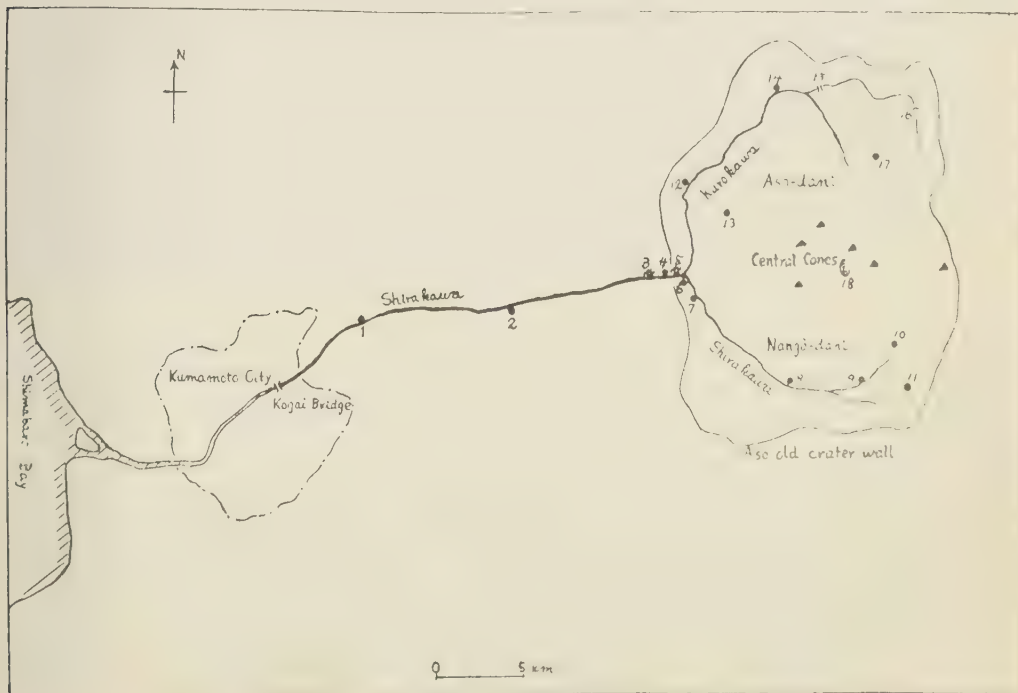


Fig. 1 The River Shirakawa and Aso crater atrio

1 Yuge, 2 Nakajima, 3 The 3rd Kurokawa power plant, 4 Tatenō, 5 The 1st Kurokawa power plant, 6 Toshita, 7 Kain, 8 Gion, 9 Ochōzu, 10 Shikimi, 11 Takamori, 12 Matoishi, 13 Nagamizu, 14 Uchinomaki, 15 Sengoku-bridge, 16 Kōjō-bridge, 17 Miyaji, 18 Mt. Aso (the present crater)





(a)



(b)



(c)



(d)



(e)



(f)

Fig. 2 The flood and mud in Kumamoto City

(a) Kami-dōri (23h 26th)      (b) Shimo-dōri (26th)      (c) Gion-bridge  
 (d) Inside of a house      (e) Kami-dōri      (f) The front of Daigeki Theater

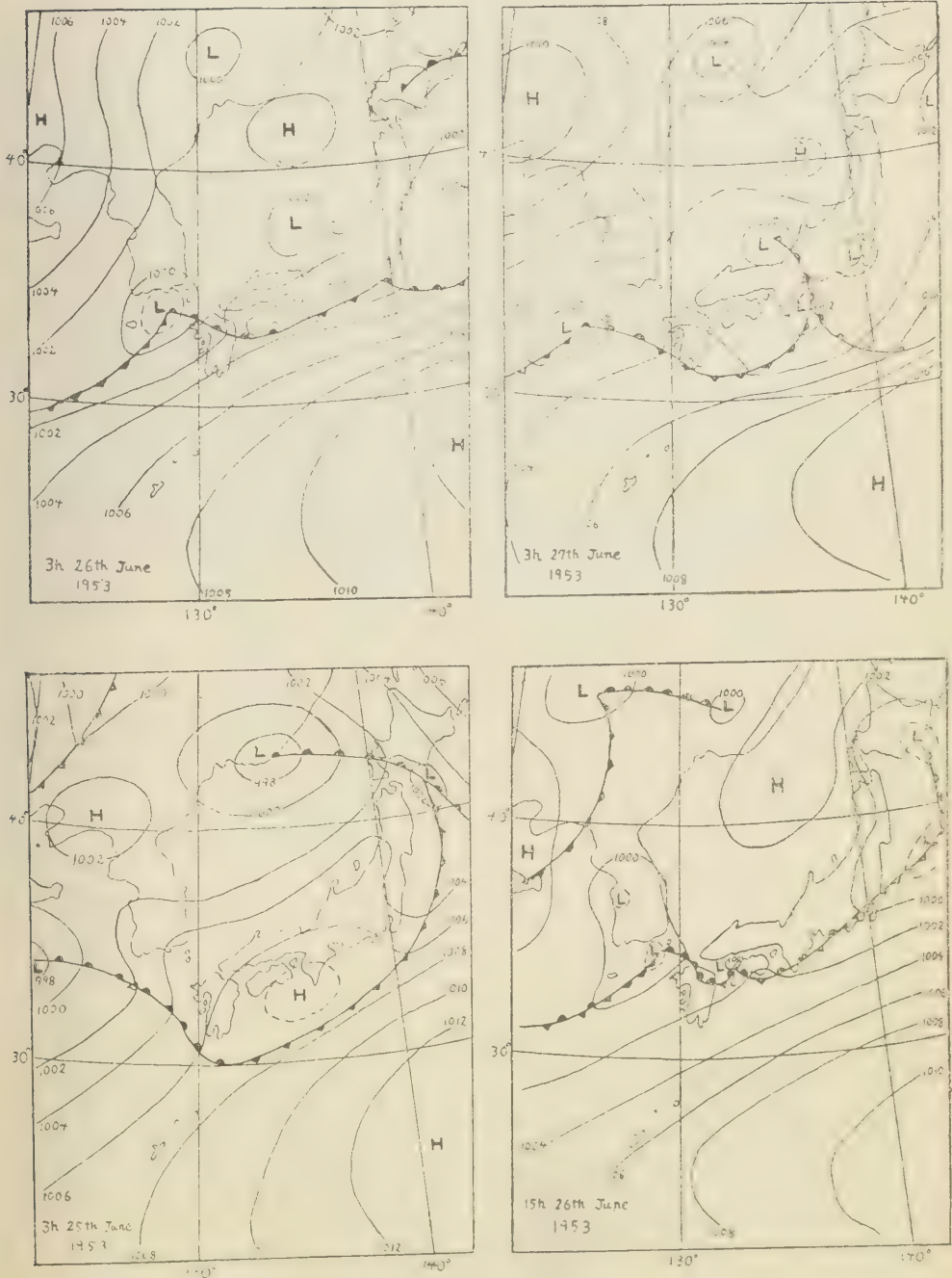


Fig. 3 Distribution of isobars

### 1. Foreword

In the case of heavy flood which was experienced in Kumamoto City on June 26-27, 1953, the water level went up about 8m above the ordinary level at Kogai-bridge over the Shirakawa which flows through Kumamoto City, and the greater part of the city was flooded. It is worthy of notice that when the flood had been over there deposited a large quantity of mud which is estimated to be several million tons. Therefore it may be said that it is a damage by mud rather than a damage by a flood.

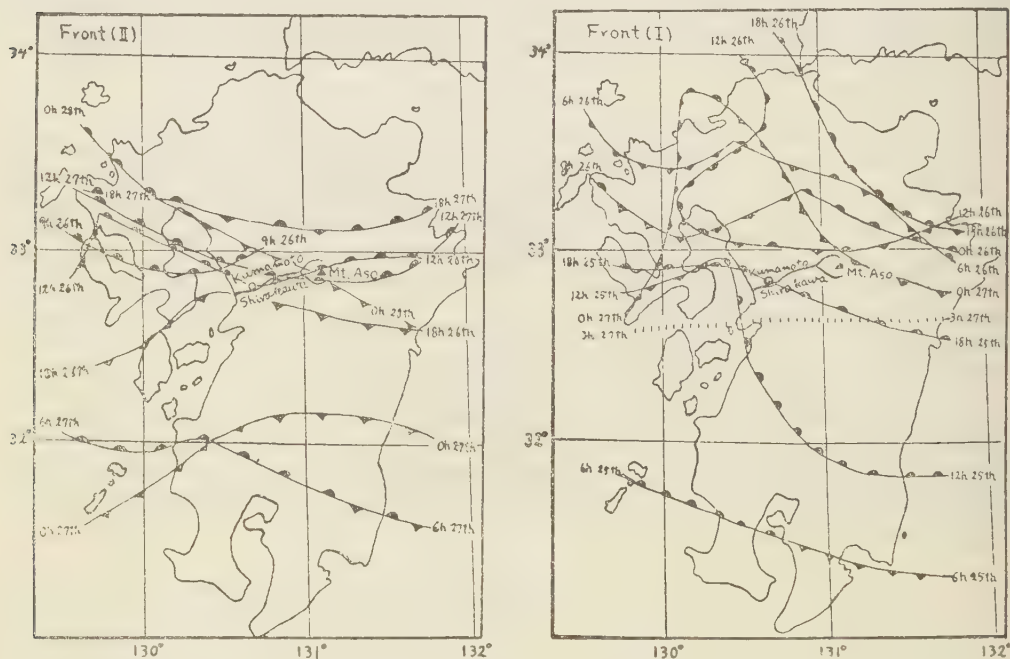


Fig. 4 Movement of Baiu-front in Kyushu

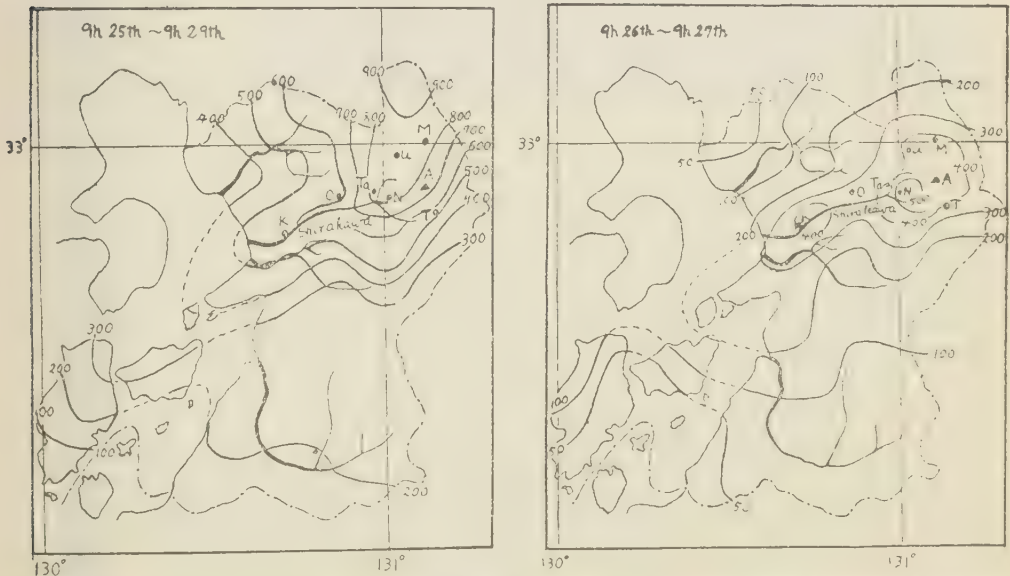
### 2. The Cause of the Flood

"Baiu" (the rainy season in Japan) had begun in this year (1953) earlier than usual and the quantity of rain was enormous. The distribution of isobars on June 25, 26 and 27, 1953 is shown in Fig. 3 [1], and the movement of Baiu front (stationary front) for the same period is shown in Fig. 4 [2].

The amount of rain was so enormous that the amount in 4 days (25-29) was about one-third of the mean yearly rainfall and the daily rainfall on 26th was comparable to the mean monthly rainfall for June (Cf. Table 1 and Fig. 5). And Baiu front having the direction EW passed over the whole catchment area of the Shirakawa twice in three days (25-27), first northwards and next southwards. Therefore it rained heavily in the whole catchment area of the Shirakawa.

Table 1 Amount of Rain (mm)

Observation point Period	Kuma- moto	Ôzu	Tateno	Nagamizu	Takamori	Uchino- maki	Miyaji	Mt. Aso
9h 26th~ 9h 27th	411.9	329.5	503.0	500.2	315.9	440.5	479.0	432.3
Mean monthly Amount for June	336.2	314.5	—	567.4	376.6	446.7	372.4	530.5
9h 25th~ 9h 29th	595.9	598.1	850.0	828.4	588.1	812.0	876.0	733.8
Mean yearly amount	1756.0	1677.3	—	2815.1	2016.0	2419.9	1985.6	2842.4



K: Kumamoto City, O: Ôzu, Ta: Tateno, N: Nagamizu, T: Takamori, U: Uchinomaki, M: Miyaji, A: Mt. Aso

Fig. 5 Distribution of the rainfall in Kumamoto Prefecture (mm)

The rainfall in the down stream basin of the Shirakawa (Kumamoto City and nighbourhood) reached the maximum about 3 hours latter than that in the upper stream basin (Aso old crater atrio) reached the maximum. (Cf. Fig. 6)



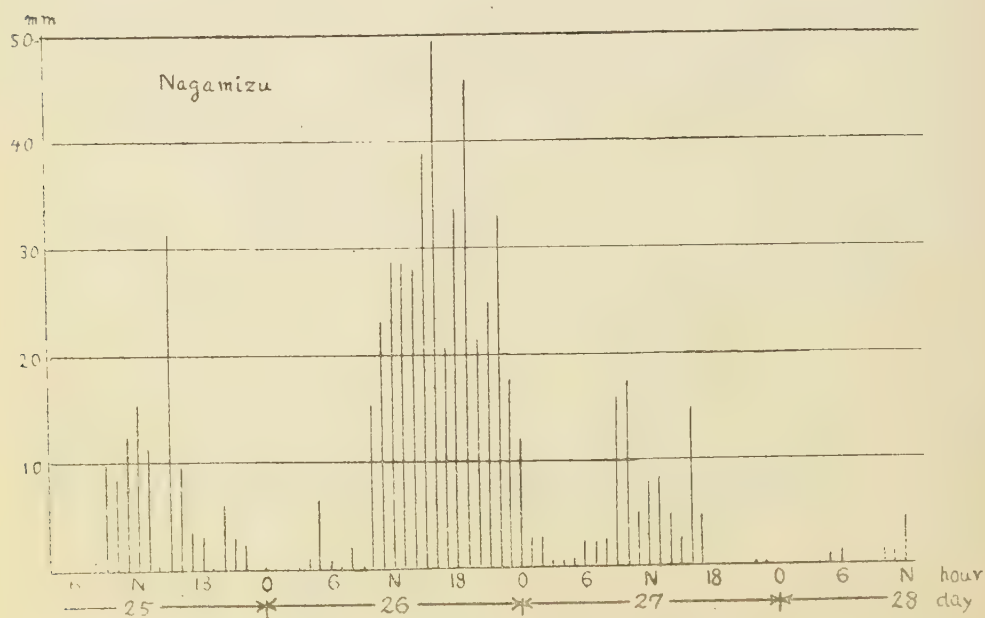
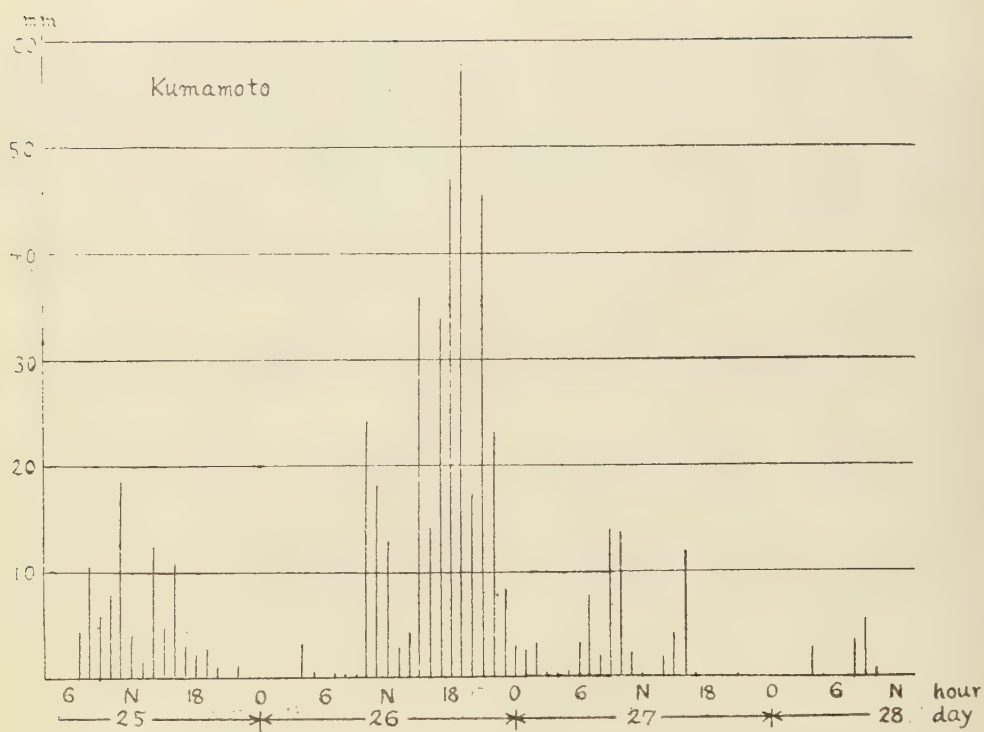
Fig. 6 Amount of Rain ( $\frac{\text{mm}}{\text{hour}}$ )





Fig. 7 Rain sculpture on the south side of Aso central cones

In consequence, the run-off due to the heavy rain in the upper stream basin overlapping on that due to the heavy rain in the down stream basin, the water level in Kumamoto City went up greatly. In addition to, a great quantity of mud due to the erosion in Aso crater atrio flowed down and deposited in Kumamoto City, so they caused serious damages.

### 3. The Time when the Highest Water Level was Observed

It is very difficult to study on this flood, because the numerical data is poor. There was no self-recording water gauge along the Shirakawa, and a few staff-gauges which man had set along the river were mostly carried away by the flood at the begining of the flood. Moreover there was no self-recording rain gauge in Nangô-dani atrio (south side of Aso central cones), but according to our researches the rainfall in Nangô-dani atrio had great influence upon the flood in Kumamoto City, of which we will mention later.

Using the results of field study, data of the remained staff-gauges and notes on the flood which were made by about 12,000 students in the flood periphery, we have been studying about the aspects of this flood since that day,

Time when the highest water level was observed

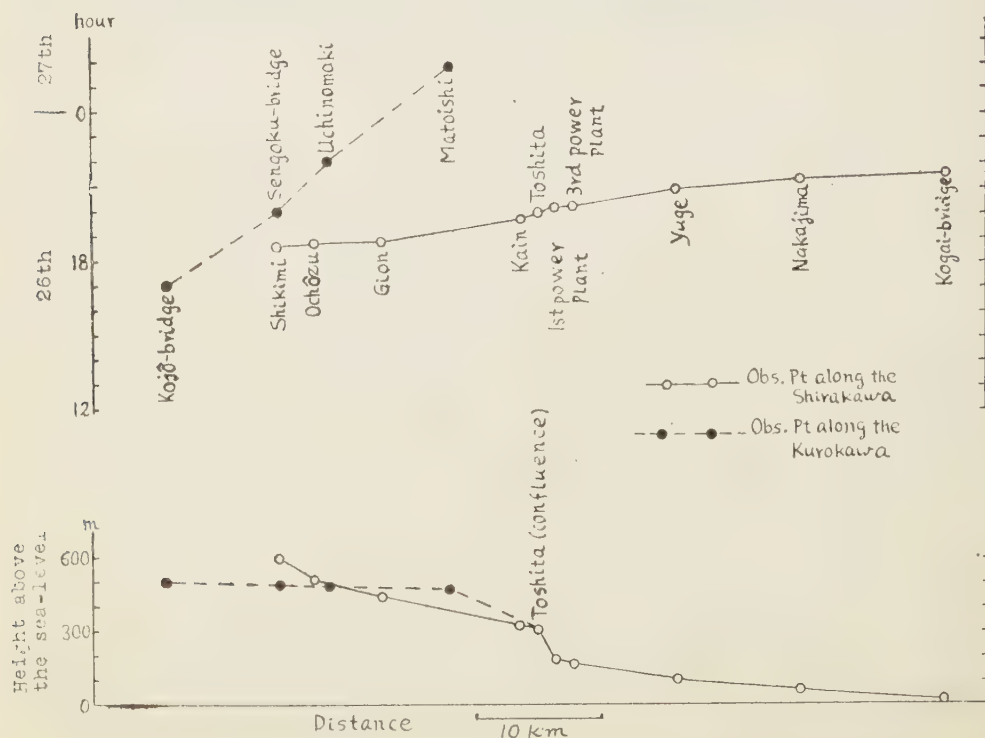


Fig. 8

At several points along the Shirakawa, the time of appearance of the highest water level was observed and a part of the results is shown in Fig. 8, and the height above the sea-level at the observation points and the distance along the river are also shown in the same Figure.

The River Kurokawa flows through Aso-dani atrio (north side of Aso central cones) and the upper part of the Shirakawa flows through Nangô-dani atrio (south side of Aso central cones), and both join at Toshita (see Fig. 1). These two rivers have a catchment area of the same order, and the intensity of the rainfall was nearly equal in both atrio this time.

Examining Fig. 8, man will find that the time of appearance of the highest water level changes continuously along the Shirakawa and there is a discontinuity in the time of appearance of the highest water level along the Kurokawa at the confluence of two rivers. It may be explained as follows. As the slope in Nangô-dani is steep, the flood in there flowed through Tateno-ravine of Aso old crater wall soon and got to Kogai-bridge (situated in the east part of Kumamoto City) about 21<sup>h</sup> 30<sup>m</sup> when the water level at Kogai-bridge reached the maximum height. On the contrary, as the slope in Aso-dani is gentle the Kurokawa overflowed and a part of Aso-dani atrio formed a natural retension reservoir; hence the flood was naturally controlled and got to Kogai bridge several hours later than that from Nangô-dani.

The facts above described tell us that the run-off due to the rainfall in Aso-dani atrio had a little influence on the flood in Kumamoto City and its influence would appear several hours late. In other words, we may say as follows. Between the rainfall in Aso old crater where is the source of the Shirakawa, the rainfall in Nangô-dani atrio had a large influence on the flood of the down stream and deposited a great quantity of mud in Kumamoto City; and that in Aso-dani atrio comparatively little influence and its influence presented about 6 hours later.

The above description may be ascertained from the fact that the land-and mountain slip and mud-flow were hard on the south side of Aso central cones and slight on the north side.

#### 4. The Highest Water Level at Kogai-bridge

The majority of bridges over the Shirakawa was washed away by the flood, but a few bridges remained and Kogai-bridge is one of the remained. Immense quantity of drift wood was caught by this bridge girder and the water level rose more, consequently the left bank of the river was broken and many people died and many houses were washed away.

We have recorded the water level of a well in the ground of Kumamoto University not far from Kogai-bridge these three years. Comparing the record with the hourly rainfall at Kumamoto, we have got the relation between the hourly rainfall and the rise of water level of the well per hour. The result tells us that there exists about seven hours phase



Fig. 9 Drift wood caught by Kogai-bridge



difference between the rain and the rise of water level. Taking into consideration this phase difference, the hourly rainfall and the corresponding rise of water level of the well per hour for 25, 26 and 27th June are shown in Fig. 10.

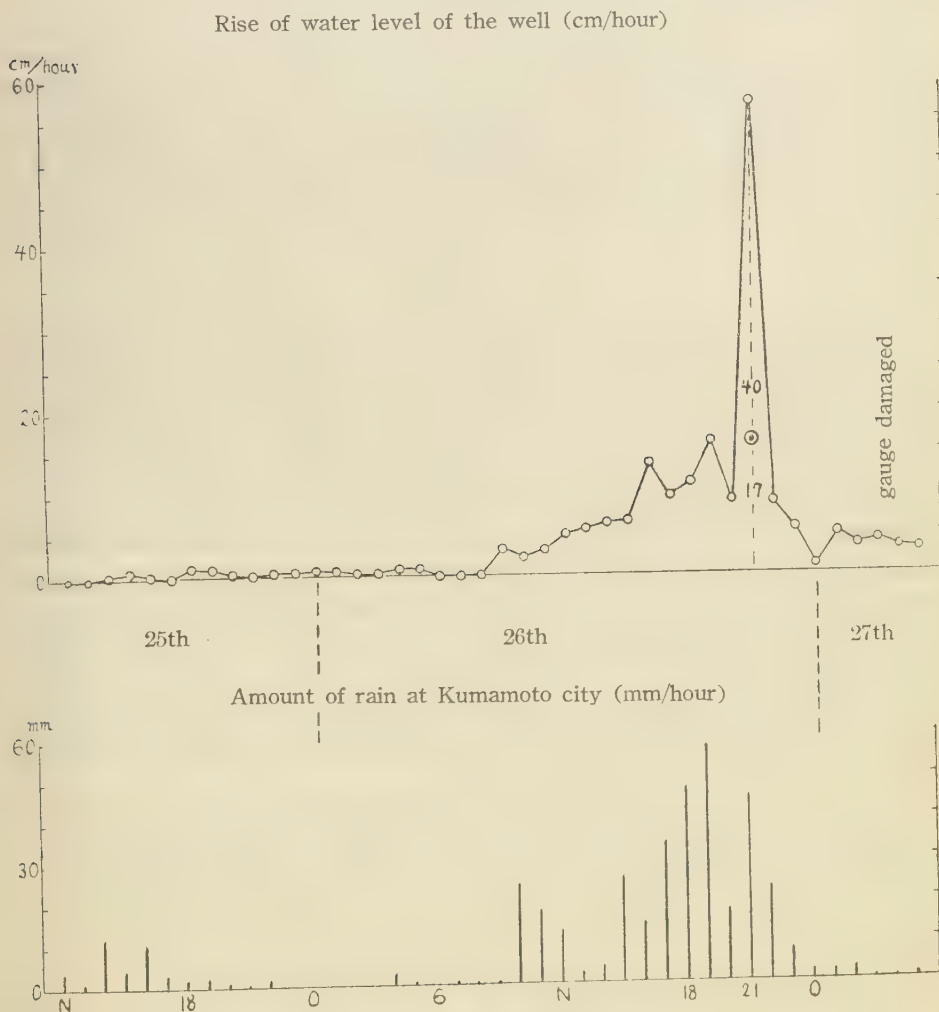


Fig. 10

If we take into consideration that it does not always rain uniformly throughout a hour, the correspondence in Fig. 10 is satisfactory except the case 21<sup>st</sup> 26th. The rise of water level for 21<sup>st</sup> is extraordinarily large and amounts to 57cm/hour. What means this large irregularity? If we assume that the rise of water level due to the rain at Kumamoto



for 21<sup>h</sup> is equal to that for 19<sup>h</sup> namely 17cm/hour. the residual  $57-17=40$  (cm/hour) may be attributed to the effect of flow from the upper stream. Moreover, owing to the observation near Kogai-bridge, the flow began suddenly to transport volcanic ashes (mud) about 20<sup>h</sup> 30<sup>m</sup> and the water level of the river reached the maximum height about 21<sup>h</sup> 30<sup>m</sup>.

A careful looking at Fig. 10 shows that there is some continuous rise of water level of the well during the period from 1<sup>h</sup> to 5<sup>h</sup> 27<sup>th</sup>. This rise which can not be attributed to the rainfall at Kumamoto, should originate from the upper stream flood. This result is in good accordance with our description in the preceeding article, which indicates that the flood from Aso-dani would appear several hours later. Here, we may again confirm that the rain in Nangô-dani has a great effect upon the flood in Kumamoto City and that in Aso-dani has a little effect.

### Conclusions

The past days. people have thought little of Nangô-dani district, concerning the problem of flood-controll and prediction. Perhaps the reason lies in a relative density of population, a means of communications and a cultural institution etc. Even though there are a few reports on study about the Kurokawa [3] and a few installations in Aso-dani, nealy none in Nangô-dani so far as the writer's knowledge is concerned.

According to the writer's investigation, the flood in Kumamoto City depends chiefly upon the rainfall in Nangô-dani and slightly upon the rainfall in Aso-dani. And mud is transported mostly from Nangô-dani. In the case of the flood on June 26-27, 1953, the flood from Nangô-dani took 2~3 hours to get to Kogai-bridge and that Aso-dani 7~9 hours. Therefore, with respect to the flood controll and prediction we must think much of Nangô-dani atrio.

In regard to the flood prediction, the flood discharge and the quantity of deposited mud, the writer will report in the following paper. This work was carried out under the support of the Scientific Research Expenditure.

In concluding this paper the writer wishes to express his hearty thanks to the following persons; to Prof. S. T. Nakamura and Prof. M. Namba for their kind giudance and encouragement, and to teachers and students who made notes about the flood.

### References

1. Kumamoto Weather Station: Urgent Report on Heavy Rain (1953)
  2. Fukuoka Meteorological Observatory: Report on Anomalous Weather No.1 (1953)
  3. Nomitsu: Geophysics Vol.6, 199, Vol. 7, 199
- Murota: Kumamoto J. Sci. A. Vol.1, No.2 (1953), 62  
etc.

# STUDIES ON THE HYDROGEN BOND (PART 1) POTENTIAL FUNCTION OF THE HYDROGEN BOND.

Kōichi KAKU

(Received February. 15, 1954)

To solve the hydrogen bond problem, potential energy of linear O-H...O system is calculated on the assumption that the potential energy can be represented by simply superposing two Morse functions, controlled by hydroxyl group in a normal state. Using thus obtained potential function, the O-H distance, the force constant and height of potential barrier was estimated with fairly good agreement with experimental values.

## 1) Potential Curve

To date not much progress has been made in the study of the quantum theory of hydrogen bond. The main theses up to the present are Gillette and Sherman's<sup>(1)</sup> quantum mechanical theory and Coggeshall's<sup>(2)</sup> semi-empirical calculation. It is quite difficult to obtain results reliable enough from calculations by quantum mechanical method. Therefore Coggeshall proceeded as follows, on assuming a physical model for hydrogen bond. He assumed that O-H distance in R-OH, which is not hydrogen bonded, is increased  $z$  on account of electronic polarization when hydrogen bond is formed. The potential of a normal hydroxyl group is assumed to be expressed by a Morse function with O-H distance as the variable. When hydrogen bond is formed, the electrostatic potential due to polarization  $-qEz$  is overlapped to the former. Here,  $q$  is the effective charge on hydrogen,  $E$  is the electric field component parallel to the direction of the valence bond at hydrogen atom and  $z$  is the displacement from equilibrium position of H-atom. Then the energy level can be found by solving the wave equation

$$\frac{d^2\psi}{dz^2} + \frac{8\pi^2\mu}{h^2} [W - D \{1 - \exp(-az)\}^2 + qEz] \psi = 0 \dots\dots\dots (1)$$

Where various notations means usually adopted ones in diatomic molecule.

The shift of wave length can be excellently explained by this scheme but neither the change in intensity nor the splitting of absorption band of carboxylic acids can be interpreted.

The splitting of infrared absorpton band may be interpreted by assuming the potential curve having two minima as in the double minima problem of ammonia molecule. The empirical evidence also supports this. Karle and Brockway<sup>3)</sup> report the O-O distance is 2.76 Å in the dimer of acetic acid, on the other hand, according to Davies and Sutherland<sup>(4)</sup> the O-H distance in the dimer is 1.04 Å. Thus H-atom is situated nearer to the one O-atom than the others. The results of Wollan's<sup>(5)</sup> study on the structure of ice by neutron diffraction indicates that Paulings's<sup>(6)</sup> model is the best. In other words, the hydrogen atom in the hydrogen bond has two equilibrium positions on the straight line joining O-O, the

H-atom existing for the same period in either of the two. These empirical evidence suggests the use of symmetrical potential curve with two minima for O-H...O. We assume, here, that the potential energy of linear O-H...O system is equal to the sum of O-H and H...O, both expressed by Morse function having same parameters with consistent variable distance between O- and H-atom. Then the potential energy  $U$  takes the form

$$U = D[1 - \exp\{-a(r - r_e)\}]^2 + D[1 - \exp\{-a(d - r - r_e)\}]^2 \dots (2)$$

where

$D$ : dissociation energy of OH supposed to be a diatomic molecule.

$a$ : a constant related to vibration frequency  $\nu$  and reduced mass  $\mu$  by

$$a = 2\pi\nu \sqrt{\frac{\mu}{2D}}$$

$d$ : O...O distance

$r_e$ : O-H distance from the one O-atom.

This formulation coincided incidentally with Huggin's<sup>(7)</sup> idea published early as 1936, but as no comparable data existed at that time his idea was forgotten, but at present it is not without worth to re-examine with new experimental data. Huggins used "modified" Morse function, but in this paper it was conducted by simpler form (2).

When  $d$  satisfies the inequality

$$\exp\left[-a\left(\frac{d}{2} - r_e\right)\right] < \frac{1}{2},$$

$U$  has two minima, but in other cases it has a single minimum. (Fig. 1.)

## 2) O-H Interatomic Distance in Dimer.

Taking the Pauling's<sup>(8)</sup> bond energy 110.2 Kcal/mol for the dissociation energy  $D$ , in conjunction with the wave number  $3584 \text{ cm}^{-1}$  for the O-H stretching vibration frequency in acetic acid given by Buswell<sup>(9)</sup>,  $a$  is found to be  $2.22 \times 10^8 \text{ cm}^{-1}$ . Assuming as the value of a constant  $r_e$  to be  $0.96 \text{ \AA}$ , which was found in ice by the neutron diffraction<sup>(5)\*</sup>. Now putting  $d = 2.56 \text{ \AA}$ , we have

$$\exp\left[-a\left(\frac{d}{2} - r_e\right)\right] \div 0.5.$$

Accordingly, if O...O distance is longer than  $2.56 \text{ \AA}$ , potential curve has minimum at two positions. O-H distance in the dimer are calculated as  $r$  which

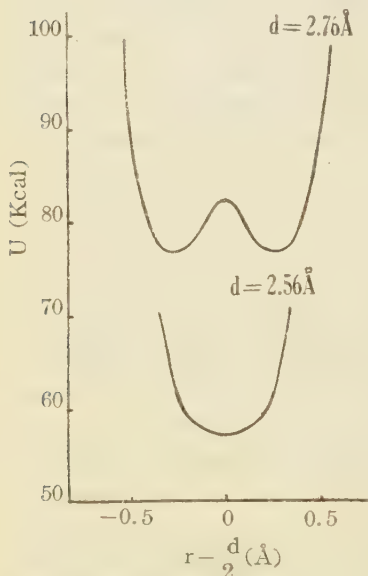


Fig1. Potential Curve of Dimer.

\* According to Williams<sup>(12)</sup> this value for formic acid is  $0.96 \pm 0.01 \text{ \AA}$ .

gives the minimum in the potential curve for various O...O distances (column 1) are shown in Table 1 (column 2). If 102 Kcal/mol is adopted for  $D$ , which is used in various text books<sup>(10)</sup>, we obtain for  $a$  the value  $2.30 \times 10^8 \text{ cm}^{-1}$ , and the corresponding values are also shown in Table 1 (column 3).

Table 1. O-H Distance of Dimer.

O-H...O distance	Calculated values ( $a=2.22 \times 10^8 \text{ cm}^{-1}$ )	Calculated values ( $a=2.30 \times 10^8 \text{ cm}^{-1}$ )	Observed value
$2.67 \times 10^{-8} \text{ cm}$	$1.09 \times 10^{-8} \text{ cm}$	$1.10 \times 10^{-8} \text{ cm}$	
2.70 "	1.08 "	1.07 "	
2.73 "	1.07 "	1.06 "	
2.76 "	1.05 "	1.03 "	$1.04 \times 10^{-8} \text{ cm}^{(3,14)}$

According to Herman<sup>(11)</sup> the O-O distance is  $2.67 \text{ \AA}$  and the shorter O-H distance is  $1.08 \text{ \AA}$ . Also according to Karle<sup>3</sup> the O-O distance is  $2.76 \text{ \AA}$  for ice,  $2.73 \text{ \AA}$  for formic acid,  $2.76 \text{ \AA}$  for acetic acid; according to Davies<sup>9</sup> the O-O distance is  $2.73 \text{ \AA}$  for formic acid and the shorter O-H distance is  $1.04 \text{ \AA}$ . In either cases the calculated value and the observed value coincide very well.

### 3) The Height of the Central Potential Hill.

The heights of the central potential hill calculated from the above data are shown in Table II. On looking at the table it can be seen that the potential hill becomes higher as  $d$  becomes greater. This seems in qualitative agreement with actual facts. For acetic acid we

Table 2. Height of Central Potential Hill

O-H...O Distance	Height of Hill ( $a=2.22 \times 10^8 \text{ cm}^{-1}$ )	Height of Hill ( $a=2.30 \times 10^8 \text{ cm}^{-1}$ )
$2.67 \times 10^{-8} \text{ cm}$	1.87 Kcal	2.45 Kcal
2.70 "	2.75 "	3.67 "
2.73 "	3.74 "	4.39 "
2.76 "	6.71 "	6.02 "

have no suitable experimental value to test this, but on scrutiny of various reports up to present the following seems worthy of note. Eyring<sup>(12)</sup> presented a mechanism, that proton jumps from one water molecule to a neighboring one in order to explain the abnormal conductance of hydrogen ion and calculated the potential hill by the theory of absolute reactions rates as the energy necessary for the jump of hydrogen from one "water molecule" to another, and he obtained the value 2.8 Kcal. Again R. Fujishiro<sup>(13)</sup> considered the anomalous dispersion of electric wave in alcohol from the standpoint of the theory of absolute reaction rates and he obtains in the same manner values 3.4 Kcal for ethyl alcohol, 4.0 Kcal for propyl alcohol, 5.0 Kcal for iso-butyl alcohol. An inspection of the table shows the calculated values are slightly higher than observed values. The O-H

distance increases from  $0.96\text{\AA}$  to  $1.04\text{\AA}$  when the hydrogen bond is formed, so the "dissociation energy", the parameter  $D$ , will naturally change. Now considering the electrostatic energy only as in Coggeshall's paper, the dissociation energy will probably decrease. Consequently the height of the potential hill also decrease.

#### 4) Force Constant.

Force constant  $f$  shows the curvature of potential curve in the equilibrium position and is given by

$$f = \frac{d^2U}{dr^2}$$

Now assuming the potential energy for stretching vibration of OH is given by a Morse function, the force constant of O-H group in monomer is calculated to be

$$f_m = 7.85 \times 10^5 \text{ dyn./cm.}$$

If the potential energy of dimer is given as before the force constant  $f_d$  for dimer is calculated to be

$$f_d = 3.26 \times 10^5 \text{ dyn./cm.}$$

As  $f_d$  is approximately  $1/2$  of  $f_m$ , the radius of curvature of dimer becomes great. Subsequently the valley of the potential will be very flat and broad, so the band of infrared absorption spectrum will be broad in width. This is in qualitative agreement with experimental fact<sup>(15)</sup>.

It is difficult in the case of dimer to compute the force constant from the experimental value but in order to make rough estimation, we shall calculate it, firstly, as a diatomic molecule.

Then the force constant  $f_1$  is

$$f_1 = 4\pi^2 c^2 \tilde{\nu}^2 \mu, \quad \begin{array}{l} \text{where } c; \text{ light velocity} \\ \tilde{\nu}; \text{ wave number} \\ \mu; \text{ reduced mass.} \end{array}$$

According to Buswell<sup>(8)</sup> the wave number of O-H stretching vibration of acetic acid dimer is  $3049 \text{ cm}^{-1}$  and  $f_1$  becomes

$$f_1 = 5.47 \times 10^5 \text{ dyn./cm.}$$

Next, we consider the system to be linear tri-atomic molecule O-H-O and for simplicity it will be supposed that hydrogen atom is centrally located in O-O. Equating the observed vibration corresponds to the valence vibration  $\nu_2$  of the antisymmetric mode, the force constant is given by



$$f_2 = 4\pi^2 c^2 \bar{\nu}^2 \frac{M_H M_o}{M_H + 2M_o} \div 2.74 \times 10^5 \text{ dyn./cm},$$

where;  $M_H$ ,  $M_o$  are masses of Hydrogen and Oxygen-atom, respectively.

Those rough estimations confirm the calculated value  $f_d$  is not far from truth.

In conclusion there would seem to be of no great mistake in taking the combination of Morse function as the potential form of the dimer.

#### 5) Acknowledgement.

In closing I wish to express my deep appreciation and gratitude to my instructor Professor Ochiai for his ever ready guidance and encouragement.

(December 12, 1953. The Paper read before the 5th Meeting of Kyushu Branch of Chemical Society of Japan.)

### References

- 1) R.H. Gillete and A. Sherman; Jour. Am. Chem. Soc., **58**, 1135 (1936).
- 2) N.D. Coggeshall; Jour. Chem. Phys., **18**, 978 (1950).
- 3) J.W. Karle and L.O. Brockway; Jour. Am. Chem. Soc., **66**, 574 (1944).
- 4) M.M. Davies and G.B.B.M. Sutherland; Jour. Chem. Phys., **6**, 755 (1938).
- 5) E.O. Wollan, W.L. Davidson and C.G. Shull; Phys. Rev., **75**, 1348 (1949).
- 6) L. Pauling; Jour. Chem. Soc., **57**, 2680 (1935).
- 7) M.L. Huggins; Jour. Phys. Chem., **40**, 723 (1936).
- 8) A.M. Buswell, W.H. Rodebush and M.F. Roy; Jour. Am. Chem. Soc., **60**, 2239 (1938).
- 9) L. Pauling; The Nature of the Chemical Bond p. 53.
- 10) Morino; Gendai-no-kagaku p. 85.  
J.C. Slater; Introduction to Chemical Physics p. 132.
- 11) R.C. Herman and R. Hofstadter; Phys. Rev., **53**, 940 (1938).
- 12) Van Zandt Williams; Jour. Chem. Phys., **15**, 232 (1947).
- 13) H. Eyring; The Theory of Rate Process p. 566.
- 14) R. Fujishiro; Jour. Japanese Chem. Soc., **70**, 229 (1950).
- 15) S. Seki; Chemistry and Chemical industry **6**, 219 (1953).





